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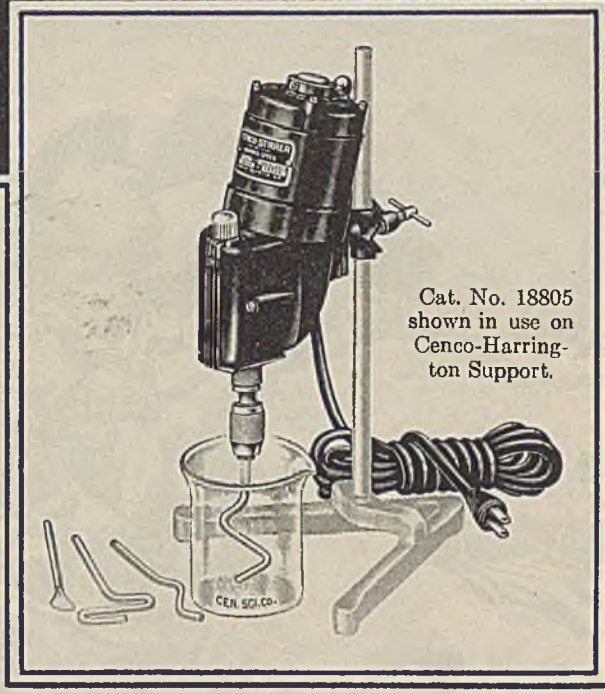

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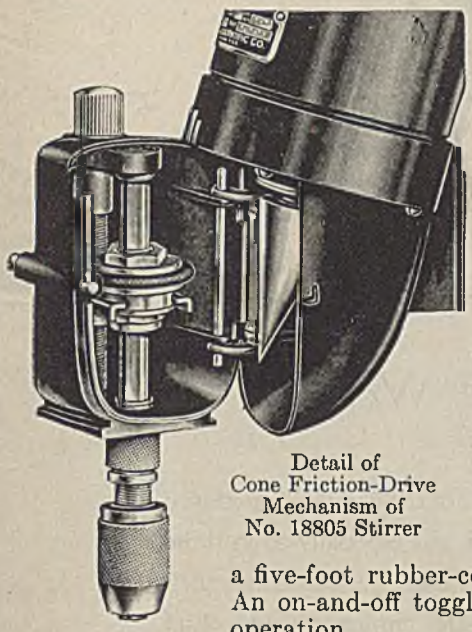

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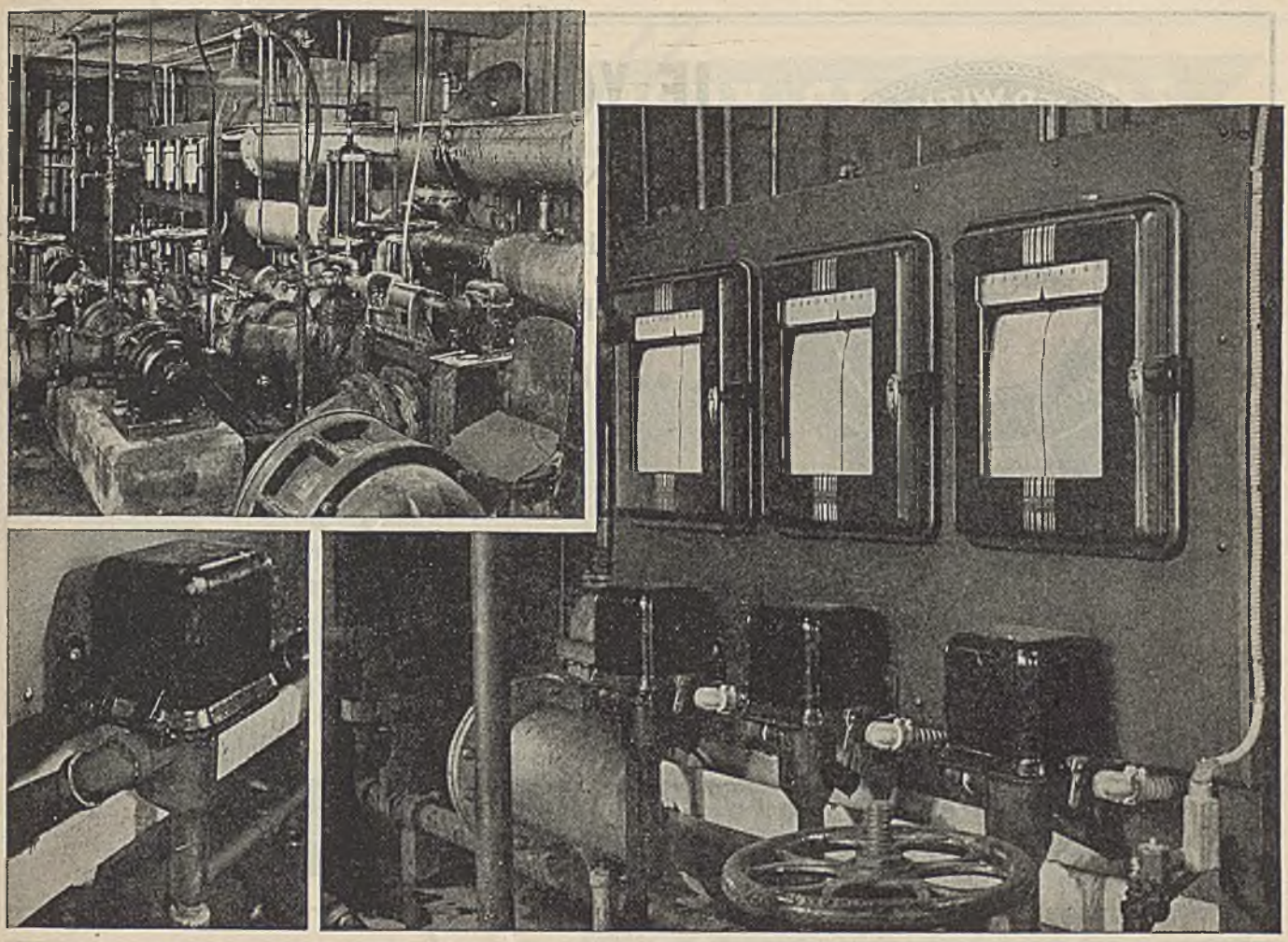

Typical views in the filter plant, Finishing Division of Arkwright Corp., Fall River, Mass. The three Micromax Recorders show, left to right, the pH of finished water at the clear well; pH of raw water coming into filter plant; pH of water just after alum and filters. Note electrode unit at left.

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Chemical Analysis by Powder Diffraction

LUDO K. FREVEL, The Dow Chemical Company, Midland, Mich.

This paper cites examples of use of the powder diffraction method in the chemical identification of solids, and discusses some of the general difficulties that may be encountered in its use.

IN THE past ten years the powder diffraction method has been used to an increasing extent in the chemical identification of solids (*4, 5, 9, 12, 13, 16, 24, 26, 30, 34, 46, 47, 59, 60, 62*). The utility of the method resides in its ability to detect the state of chemical combination for each crystalline component in a mixture (*30*). The present paper cites a few typical examples and discusses some of the general difficulties that may be encountered in this physical method of chemical analysis.

Identification of boiler deposits is a general problem that is conveniently handled by the powder method. A particular scale submitted for identification was examined by chemical analysis, by microscopic examination, and by powder diffraction. Table I lists the data ascertained by each method.

The information obtained by the diffraction method is of evident value to the chemist interested in selecting the correct treatment for the removal of scale or in devising methods to diminish scaling. The manner in which the diffraction data are conveniently compared with published powder data is illustrated in Table II.

Other typical problems solved by the diffraction method are: the identification of corrosion products, the constitution of fluxes, the detection of pigments or fillers in plastics or elastomers, the analysis of minerals, the recognition of allotropic modifications, and the study of chemical reactions in the solid state.

As illustrated in Table II, chemical analysis by the powder method consists of matching the diffraction pattern of an unknown material with one or more standard powder patterns. This requires (1) a correct registration and measurement of the diffraction lines and (2) a careful interpretation and evaluation of these data as applied to chemical analysis. The first part of the problem has received considerable attention in the literature and only a few points require enumeration. The second part, however, has not been treated extensively in previous publications and deserves detailed discussion.

COMPLICATIONS IN REGISTRATION OF POWDER DIFFRACTION PATTERNS

ABSORPTION EDGES. In view of the fact that most x-ray diffraction work is being done with filtered radiation, characteristic

Table I. Data on Boiler Scale

Chemical Analysis	%	Microscopic Analysis	Powder Diffraction Analysis	%
Fe	28.32	Black shiny powder, heterogeneous; particles too small for refractive index measurements		~40 $FeFe_2O_4$
Ca	22.30			~30 $CaCO_3$, calcite
S	6.21			~30 $CaSO_4$
CO_3--	22.10			
Ignition loss	15.70			
		Advantages		
Accurate quantitative data, method of analysis independent of state of aggregation of sample		High sensitivity for detecting minor phases, morphological details readily ascertainable (*29*)	Direct identification of compounds, nondestructive method applicable to extremely fine powders	

Table II. Powder Diffraction Data on Boiler Scale

Filtered MoKα radiation used to obtain powder diffraction patterns. d = interplanar spacing measured in Å. I = peak intensity of a diffraction line as estimated with a direct comparison intensity scale (arbitrary units). I/I_1 = relative intensity of a diffraction line, where I_1 is intensity of strongest line of particular phase in question. Most representative value for I_1 of phase 1 is taken as 33 and is obtained by multiplying intensities of six unambiguous reflections (4.83, 2.95, 2.41, 1.705, 0.967, 0.855 Å.) by corresponding relative intensities of $FeFe_2O_4$ and taking arithmetic mean of computed values of I_1 (36, 55, 37, 22, 25, 20). The average value for the strongest line of phase 2 is 22; for phase 3 it is 38.

Spectroscopic analysis of scale: Fe, Ca, chief constituents; Co, Mo, Cu, Na, 0.001 to 0.01%.

Boiler Scale		$FeFe_2O_4$		Phase 1	$CaSO_4$		Phase 2	$CaCO_3$		Phase 3	
d, Å.	I	d, Å.	I/I_1	I/I_1	d, Å.	I/I_1	I/I_1	d, Å.	I/I_1	I/I_1	ΣI
5.80	1	..	..	..	..	..	..	..	..	..	..
4.83	3	4.85	0.06	0.09	..	..	..	..	..	..	..
3.87	4	..	..	..	3.89	0.03	(1)	3.86	0.08	(3)	4
3.49	25	..	..	..	3.49	1.00	1.14	..	..	..	..
3.03	30	..	..	..	..	..	..	3.04	1.00	0.79	..
2.95	10	2.97	0.28	0.30	..	..	..	..	..	..	..
2.84	15	..	..	..	2.85	0.67	0.68	..	..	..	..
2.52	75	2.53	1.00	(33)	..	..	..	2.49	0.20	(8)	41
2.41	6	2.42	0.11	0.18	..	..	..	..	..	..	..
2.33	8	..	..	..	2.32	0.33	0.36	..	..	..	..
2.27	10	..	..	..	2.26	0.01	(0.2)	2.28	0.24	0.26	..
2.21	8	..	..	..	2.20	0.33	0.36	..	..	..	..
2.08	30	2.10	0.32	(11)	2.08	0.11	(2)	2.09	0.20	(8)	21
1.99	1	..	..	..	1.99	0.11	(2)	..	..	..	..
1.91	10	..	..	..	1.93	0.04	(1)	1.92	0.32	0.24	..
1.865	12.5	..	..	..	1.86	0.27	(6)	1.87	0.24	(9)	15
1.745	4	..	..	..	1.74	0.20	0.18	..	..	..	..
1.705	6	1.71	0.16	0.18	..	..	..	..	..	..	..
1.640	4	..	..	..	1.64	0.27	0.18	..	..	..	..
1.606	20	1.61	0.64	(21)	1.59	0.03	(1)	1.60	0.16	(6)	28
1.560	1	..	..	..	1.56	0.05	0.05	..	..	..	..
1.518	6	..	..	..	1.52	0.07	(2)	1.51	0.12	(5)	7
1.480	30	1.483	0.80	(26)	1.487	0.08	(2)	1.475	0.05	(2)	30
1.439	4	..	..	..	..	..	..	1.439	0.08	0.11	..
1.420	1	..	..	..	1.420	0.08	(2)	1.425	0.05	(2)	4
1.320	2	1.326	0.06	(2)	1.318	0.09	(2)	1.350	0.03	(1)	5
1.278	6	1.279	0.20	(7)	1.275	0.09	(2)	..	..	..	9
1.210	2	1.210	0.05	(2)	1.215	0.05	(1)	..	..	..	3
1.150	2	..	..	..	..	..	..	1.150	0.05	0.05	..
1.120	2	1.121	0.10	0.06	..	..	..	..	..	..	..
1.090	7	1.092	0.32	0.21	..	..	..	..	..	..	..
1.047	6	1.049	0.10	(3)	..	..	..	1.045	0.06	(2)	5
1.010	2	..	..	..	..	..	..	1.011	0.03	0.05	..
0.967	4	0.970	0.16	0.12	..	..	..	..	..	..	..
0.938	2	0.940	0.06	0.06	..	..	..	..	..	..	..
0.879	2	0.880	0.10	0.06	..	..	..	..	..	..	..
0.855	4	0.859	0.20	0.12	..	..	..	..	..	..	..
0.850	1	0.853	0.08	0.03	..	..	..	..	..	..	..
0.810	1	0.814	0.10	0.03	..	..	..	..	..	..	..

Table III. Preparation of Powder Specimens

Method of Preparing Powder Specimen	Precautions to Be Observed				
Grinding or filing	Influence of atmosphere (H_2O, O_2, CO_2, dust.) Grind and load sample in a drying box flushed with purified dry N_2; or grind sample under dry benzene and load wet powder into a thin-walled glass capillary (*31*, *63*)	Abrasion contamination Grind hard nonferrous materials in an agate mortar. (Micromicronizer may be useful in the pulverization of abrasives.) Remove metallic iron contamination from steel mortar by magnetic methods	Mechanical strain Vacuum-anneal metallic filings at suitable temperature (*31*)	Volatilization Grind sample containing sublimable substances in a small closed system or in an equilibrium - atmosphere [NH_4HCO_3, $(NH_4)_2CO_3$, NH_4OCONH_2, NH_4N_3, NH_4CN, NH_4SH, etc.; ammonates or alcoholates may lose NH_3 or ROH on grinding]	Phase decomposition (Supersaturated solid solutions, quenched alloys, pressure-sensitive substances such as wurtzite or brookite chemical reaction in solid state (*14*, *58*). For alloys a structure-integrating camera of micro design may be adaptable
Precipitation or crystallization	Coprecipitation or co-crystallization Make qualitative spectroscopic analysis and spot tests on washed precipitate	Oxidation Load precipitate in wet condition—e.g., pyrophoric catalysts such as Raney nickel	Solvation Vacuum-dry washed precipitate	.....	.....
Condensation, electrodeposition, or sputtering	Preferred orientation Check condensed film for preferred orientation of crystallites by taking exposures at various inclinations	Oxidation (Adsorbed O_2, H_2O, etc., on substrate)	.....	.....	.....

Table IV. Powder Diffraction Pattern of Magnesium Oxide

(hkl)	$d_{obs.}$	$d_{calcd.}$	$(I/I_1)_{obs.}$	$(I/I_1)_{calcd.}$
111	2.425	2.428	0.08	0.08
200	2.103	2.103	1.00 (50)	1.00
220	1.487	1.487	0.50 (25)	0.55
311	1.268	1.268	0.04	0.06
222	(1.216)	1.214	0.12 (6B)	0.15
400	(1.053)	1.052	0.04 B	0.06
331	(0.9661)	0.9649	0.01 B	0.03
420 α_1	0.9405	0.9405	....	..
420 α_2	0.9404	0.9405	....	..
422 α_1	0.8583	0.8585	....	..
422 α_2	0.8587	0.8585		

Type B1: $a = 4.206 \pm 0.001$ Å. (25° ± 3° C.)

Exposure. Filtered MoKα radiation; camera radius, 20.477 ± 0.010 cm., calibrated with spectroscopically pure Mg (a = 3.2026 Å., c = 5.1998 Å. at 25° C.); slit dimensions, 0.2 × 5 × 50 mm.; specimen radius, 0.2 mm.; duplex film without intensifying screen.

Preparation of MgO. Sublimed magnesium metal, spectroscopically pure, was dissolved in ≈10% HCl (c.p. grade distilled). Magnesium hydroxide was precipitated by dropwise addition of freshly prepared c.p. ammonium hydroxide. The precipitate was washed twice by decantation, followed by filtration and washing. The wet hydroxide was transferred to a clean ignited sillimanite crucible and vacuum-dried over $Mg(ClO_4)_2$. The $Mg(OH)_2$ was then converted to MgO by heating to 890° C. for 1 hour in an oxygen atmosphere free of carbon dioxide.

Chemical Analysis. % Mg = 60.22 ± 0.05 (pyrophosphate method); calcd. % Mg = 60.32.

Spectroscopic Analysis for Impurities. Si 0.01 to 0.1%, Al 0.005 to 0.05%, B 0.001 to 0.005%, Cu 0.001 to 0.005%.

Particle Size Distribution. Electron microscope, 200 to 1200 Å.; average diameter 650 Å., very uniform; particles are not of regular shape, though crystalline in character; general tendency is for platelike particles ~200 Å. thick (see Figure 1).

x-ray absorption manifests itself in four ways: (1) in the silver bromide emulsion (AgK_∞ = 0.4845 Å., BrK_∞ = 0.9181 Å.); (2) in the filter (*17*) (ZrK_∞ = 0.6874 Å., NiK_∞ = 1.484 Å.); (3) in the specimen containing elements, the characteristic absorption edges of which fall within the transmitted background radiation; and (4) in the tungsten contamination of the target (WL_1 = 1.022 Å.) (*2*). There also exists the possibility that the zinc edge (1.281 Å.) may introduce a discontinuity in the response of fluorazure intensifying screens. For powder diffraction work these effects are observed only for the more intense reflections. For example, using a sealed-off Mo tube operated at 35 kv., one finds that the intense (111) reflection of cubic silver iodide produces one spectrum toward the longer wave-length end of AgK_∞ and another corresponding to IK_∞. In the case of silver phosphate the intense portion of the continuous spectrum from (210) is slightly stronger than the (220) MoKα reflection. For powder patterns the sharpness of the edge of the transmitted spectrum is often blurred; consequently care must be exercised in distinguishing these edges from weak Kα reflections.

Fluorescence. Fluorescence excited in the sample by primary Kα radiation is readily detected by a general enhancement of the background and a corresponding decline in the prominence of the desired diffraction pattern. Using MoKα radiation for specimens containing yttrium, strontium, rubidium, bromine, or selenium, one obtains relatively weak diffraction patterns with high background. For example, carbon tetrabromide gives an extremely poor powder pattern with MoKα but a normal intense pattern with CuKα. Specimens containing elements of high atomic number—e.g., gold, mercury, thallium, lead, bismuth—show L-fluorescence with MoK. These fluorescence considerations apply not only to filtered Kα radiation but also to crystal-monochromatized x-rays. In the case of filtered x-rays, the distribution of the continuous radiation may noticeably affect fluorescence. Thus if a zirconium oxide screen is placed in front of the film to filter the diffracted MoK radiation, the resultant diffraction pattern from a molybdenum specimen has a background 3.5 times as high as in the case when the filter is placed in front of the slit system. For general routine analysis by powder diffraction, two sources of Kα radiation—e.g., MoKα and CuKα—are usually adequate to avoid serious cases of fluorescence.

Resolution. The geometrical factors deciding the resolution of a Debye-Scherrer-Hull pattern are: R, radius of the camera; r, radius of the powder specimen; h, length of the specimen; δ, divergence of the impinging x-ray beam; and σ, difference in wave length of the Kα doublet. For a fixed camera radius the optimum resolution corresponds to the limiting condition: $r, h, \delta, \sigma \rightarrow 0$. In general, however, the hardness of the primary radiation used and the time required for the registration of a good diffraction pattern are the limiting factors in the design of a suitable camera.

The geometrical resolution for a camera of radius R can be expressed approximately as the sum of δ, the divergence of the diffracted beam due to the divergence or convergence of the impinging primary beam, and $\omega_{r,h}$, the angular spread of the diffracted beam due to the dimensions of the powder specimen ($\omega_{r,o} = \frac{2r}{R}$ radian, for parallel x-rays) (*8*, *32*, *41*). Accordingly, two powder reflections d and $(d + \Delta d)$ will be resolved if

$$(\Theta\alpha_2 - \Theta\alpha_1)_d < (\Theta_d - \Theta_{d+\Delta d})_\alpha > (\delta + \omega_{r,h})\Theta$$

where Θ is the Bragg angle for the interplanar spacing, d, and α denotes the wave length under consideration (*33*). For example, with MoKα_1 radiation the two powder reflections corresponding to 2.260 Å. and 2.274 Å. will be separated by 3.4′, which interval is equal to the MoKα doublet separation, $(\Theta\alpha_2 - \Theta\alpha_1)_{2.28}$. Evidently the use of very narrow slits does not aid greatly in the resolution of a noncubic powder pattern because of the disturbing doublet separation. (The utility and precision of powder diffraction work would be greatly enhanced if an intense source of strictly monochromatic $WL\alpha_1$ could be made available for precision-focusing cameras). Convenient standards for testing and calibrating powder cameras are 200-mesh powders of the following substances: pure fused magnesium oxide, pure crystallized silicon, annealed 99.9% molybdenum metal, c.p. thallous chloride, and indium sesquioxide prepared by the direct oxidation of 99.95% indium metal.

Absorption. The intensity distribution of a powder diffraction line is markedly influenced by absorption in the powder

Table V. Ambiguities Arising from Solid Solution or Isomorphism

Diffraction patterns taken with filtered MoKα radiation. d = interplanar spacing; I/I_1 = relative intensity

Substance															
Pb	d, Å.	2.85	2.47	1.74	1.490	1.428	1.134	1.105							
	I/I_1	1.00	0.50	0.50	0.50	0.17	0.17	0.17							
85Pb.15Na	d, Å.	2.85	2.47	1.74	1.487	1.424	1.131	1.102							
	I/I_1	1.00	0.37	0.20	0.31	0.07	0.07	0.07							
	Examples: In, In-Ag; Mg, Mg-In; Pd, Pd-Ag; Fe, Fe-Cr														
Ag	d, Å.	2.36	2.04	1.445	1.232	1.179	1.022								
	I/I_1	1.00	0.53	0.27	0.53	0.05	0.01								
Au	d, Å.	2.35	2.03	1.440	1.227	1.173	1.019								
	I/I_1	1.00	0.53	0.33	0.40	0.09	0.03								
	Examples: Co, Ni; Cr, Fe; Pd, Pt; Rh, Ir; Mo, W; Cb, Ta														
CuCl	d, Å.	3.12	2.70	1.91	1.63	1.353	1.240	1.104							
	I/I_1	1.00	0.08	0.60	0.30	0.06	0.08	0.06							
β-ZnS	d, Å.	3.12	2.69	1.91	1.63	1.353	1.242	1.104							
	I/I_1	1.00	0.05	0.75	0.50	0.05	0.18	0.15							
	Examples: NaBr, PbS; NaCl, Ag(Cl, Br); KCN, RbCl; Mg_2Sn, Mg_2Pb; FeF_2O_4, $NiMn_2O_4$, $ZnFe_2O_4$; Er_2O_3, Y_2O_3														
ZnF_2	d, Å.	3.33	2.60	2.35	2.27	2.10	1.75	1.67	1.56	1.492	1.412				
	I/I_1	1.00	0.80	0.06	0.20	0.05	0.80	0.20	0.08	0.11	0.32				
CoF_2	d, Å.	3.37	2.64	..	2.30	..	1.75	1.67	1.58	1.496	1.420				
	I/I_1	1.00	0.86	..	0.29	..	0.86	0.29	0.14	0.14	0.14				
SnO_2	d, Å.	3.34	2.64	2.36	2.30	2.11	1.75	1.67	1.58	1.492	1.435				
	I/I_1	1.00	0.63	0.18	0.03	0.02	0.63	0.10	0.05	0.10	0.10				
$(NH_4)_2CrO_4$	d, Å.	5.6	4.80	3.91	3.74	3.65	3.45	3.18	2.94	2.84	2.77	2.32	2.01	1.87	
	I/I_1	0.62	1.00	0.35	0.10	0.10	0.40	0.75	0.40	0.20	0.10	0.62	0.15	0.05	
$(NH_4)_2SeO_4$	d, Å.	5.5	4.80	3.89	..	..	3.45	3.17	2.95	..	2.75	2.33	1.98	1.87	
	I/I_1	0.60	1.00	0.40	..	..	0.40	0.80	0.40	..	0.20	0.40	0.20	0.10	
$CoCl_2.6H_2O$	d, Å.	5.6	4.85	3.52	3.11	2.94	2.73	2.56	2.40	2.20	2.07	2.02	1.98	1.89	1.86	1.81
	I/I_1	1.00	1.00	0.31	0.10	0.63	0.50	0.20	0.63	0.50	0.05	0.03	0.31	0.20	0.10	0.03
$NiCl_2.6H_2O$	d, Å.	5.5	4.85	3.53	3.08	2.95	2.70	2.54	2.40	2.18	2.05	2.02	1.97	1.90	1.86	1.81
	I/I_1	1.00	1.00	0.50	0.04	0.50	0.50	0.30	0.50	0.50	0.06	0.06	0.20	0.20	0.14	0.02
	Examples: $CoSO_4.H_2O$(?), $ZnSO_4.H_2O$, $NiSO_4.7H_2O$, $ZnSO_4.7H_2O$ $Co(NH_4)_2(SO_4)_2.6H_2O$, $Fe(NH_4)_2(SO_4)_2.6H_2O$, $Zn(NH_4)_2(SO_4)_2.6H_2O$, $Cu(NH_4)_2(SO_4)_2.6H_2O$														

specimen (*48, 49*). With an essentially parallel x-ray beam and a suitable combination of absorption coefficient and diameter of the powder rod, the resulting diffraction lines for low values of θ can appear as pseudo-doublets (*40*). For MoKα radiation and a specimen radius of 0.2 mm., only the denser powders containing elements of high atomic number exhibit this effect—e.g., mercuric bromide, tungsten, bismuth, etc. Dilution with flour or reducing the specimen diameter will overcome this complication. The standard wedge technique used in many laboratories does not lead to pseudo-doublets.

PREPARATION OF SPECIMEN. The two most common factors influencing the quality of a powder diffraction pattern are particle size distribution and instability of the sample. The grating limitations of a powder specimen are manifested in the breadths of the resulting diffraction lines (*10*). Thus materials of colloidal

Table VI. Partial Ambiguities Due to Isomorphism

d = interplanar spacing; I/I_1 = relative intensity. In the case of mixtures the above differences are more difficult to check

Substance													
$ZnSO_4.H_2O$	d, Å.	4.80	3.80	3.40	3.06	2.52	2.40	2.34	2.19	2.10	2.05	1.97	1.91
	I/I_1	0.64	0.11	1.00	0.40	0.40	0.06	0.11	0.14	0.10	0.05	0.13	0.08
$MgSO_4.H_2O$	d, Å.	4.82	..	3.38	3.07	2.55	2.40	2.33	2.19	2.10	2.05	1.97	1.90
	I/I_1	0.40	..	1.00	0.20	0.40	0.05	0.03	0.05	0.04	0.17	0.05	0.05
$MgSO_4.7H_2O$	d, Å.	5.9	5.3	4.50	4.22	3.76	3.41	2.96	2.87	2.74	2.66	2.48	2.38
	I/I_1	0.20	0.20	0.08	1.00	0.10	0.12	0.18	0.20	0.08	0.40	0.02	0.05
$ZnSO_4.7H_2O$	d, Å.	..	5.3	4.50	4.20	3.76	3.44	2.99	2.87	2.75	2.66	2.50	2.37
	I/I_1	..	0.60	0.16	1.00	0.20	0.30	0.12	0.30	0.10	0.25	0.12	0.08
$CoCo_2O_4$	d, Å.	4.68	2.86	2.43	2.34	2.02	..	..	1.65	1.56	..	1.432	1.235
	I/I_1	0.08	0.20	1.00	0.06	0.13	..	..	0.04	0.25	..	0.30	0.02
$ZnAl_2O_4$	d, Å.	..	2.85	2.44	..	2.02	1.91	1.85	1.65	1.55	1.480	1.431	1.232
	I/I_1	..	0.53	1.00	..	0.07	0.07	0.07	0.13	0.33	0.07	0.40	0.07
$Mn_2Al_2(SiO_4)_3$	d, Å.	2.89	2.59	2.46	2.36	2.27	2.10	2.04	1.88	1.67	1.60	1.545	1.44
	I/I_1	0.30	1.00	0.02	0.20	0.13	0.15	0.05	0.25	0.15	0.30	0.40	0.085
$Mg_3Al_2(SiO_4)_3$	d, Å.	2.88	2.58	2.45	2.35	2.26	2.10	2.03	1.87	1.66	1.595	1.54	1.440
	I/I_1	0.50	1.00	0.18	0.20	0.20	0.15	0.02	0.25	0.13	0.40	0.63	0.13
$(NH_4)Al(SO_4)_2.12H_2O$	d, Å.	7.0	5.4	4.97	4.30	4.07	3.67	3.26	3.05	2.95	2.79	2.60	..
	I/I_1	0.30	0.60	0.30	0.80	0.60	0.40	1.00	0.30	0.08	0.12	0.12	..
$KAl(SO_4)_2.12H_2O$	d, Å.	7.0	5.4	4.96	4.29	4.05	3.65	3.24	3.03	2.93	2.78	2.58	..
	I/I_1	0.04	0.20	0.08	1.00	0.40	0.04	0.40	0.16	0.12	0.20	0.06	..
$KCr(SO_4)_2.12H_2O$	d, Å.	7.0	5.5	4.98	4.31	4.08	3.68	3.26	3.04	..	2.81	2.59	..
	I/I_1	0.12	0.16	0.08	1.00	0.30	0.60	0.35	0.30	..	0.12	0.06	..
$K_2CaFe(CN)_6$	d, Å.	6.0	5.1	4.60	3.72	3.64	3.07	2.85	2.57	2.35	2.30	2.13	2.06
	I/I_1	0.07	0.30	0.03	0.13	1.00	0.10	0.03	0.42	0.03	0.10	0.07	0.10
$K_2CuFe(CN)_6$	d, Å.	..	5.1	..	..	3.63	3.06	2.86	2.57	2.36	2.29	2.13	2.06
	I/I_1	..	0.38	..	..	1.00	0.20	0.08	0.75	0.15	0.31	0.25	0.63
As_4O_6	d, Å.	6.3	3.18	2.75	2.53	2.24	2.12	1.95	1.66	1.59	1.54	1.438	..
	I/I_1	0.56	1.00	0.24	0.32	0.08	0.16	0.24	0.16	0.08	0.16	0.08	..
$Sb_2As_2O_6$	d, Å.	6.4	3.18	2.75	2.52	2.24	2.11	1.95	1.66	1.58	1.54	1.430	..
	I/I_1	0.25	1.00	0.25	0.13	0.02	0.04	0.30	0.30	0.06	0.10	0.07	..

subdivision, such as coprecipitated oxides of the spinel type, specially prepared catalysts, or clays give rather diffuse diffraction patterns that may appear insignificant in the presence of an intense sharply defined pattern. A similar situation is encountered in the field of high polymers. In order to obtain information of greater value in the case of these idiosyncracies, the use of crystal-monochromatized radiation has been advocated by a number of diffractionists.

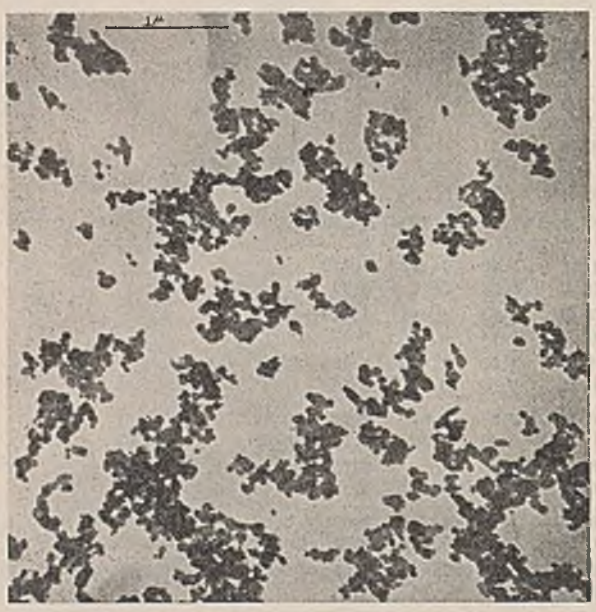

Figure 1. Electron Micrograph of Magnesium Oxide Standard

The problem of the instability of a sample usually can be overcome without serious difficulty (see Table III). Hygroscopic substances are readily powdered in a drying box and loaded into thin-walled glass capillaries that can be sealed easily. Efflorescent materials can be loaded wet (to prevent extreme crystal growth, a little amorphous material, either starch or charcoal, is admixed with the wet powder). In the case of complex organic compounds the existence of two or more allotropic modifications must be kept in mind; thus a material crystallized from a melt may give an entirely different powder pattern than the same substance crystallized from a solution. Other cases of less general occurrence are: allotropic transformation on grinding or filing (wurtzite, brookite, supersaturated solid solutions); photosensitivity (BaN_6, P_4); and chemical interaction of the substance with glass capillaries [acid fluorides, such as NH_4FHF to form $(NH_4)_2SiF_6$]. Polystyrene capillaries, developed for the study of acid fluorides, have proved useful for powder diffraction with soft radiation such as $CuK\alpha$ and $FeK\alpha$.

COMPLICATIONS IN METHOD OF ANALYSIS

Chemical analysis by the Debye-Scherrer-Hull method consists of matching the diffraction pattern of an unknown material with one or more standard powder patterns. When a match is found (see Table II) one infers that compounds $A, B, C \ldots$ are present in the unknown. If p denotes the powder diffraction data of the unknown material; p_r, the diffraction data of all the cataloged standard patterns; and Ω', the composite operation of matching the unknown with the standards $A, B, C \ldots$ one may express the mode of analysis symbolically as

$$\Omega'(p.p_r) \supset A, B, C \ldots$$

The uniqueness of this inference is not evident and requires further examination.

Validity of Standard Patterns. It is convenient to consider first the validity of the standard patterns, p_r (*4*, *25*, *26*). From the results of x-ray diffraction analysis it is well recognized that the powder diffraction pattern of a single phase is a function of the particular crystal structure, the elements present, and the crystallite-size distribution of the powder. To be acceptable as a standard each substance should be subjected to a precise analysis to substantiate the assigned chemical formula. The method of preparation of the powder specimen should also be stated. Table IV illustrates a satisfactory presentation of a powder diffraction standard.

On examining the published tabulated powder data (*4*, *25*, *26*) one finds the labeled standards usually have not been examined for the correctness of the ascribed chemical formulas. This deficiency was realized when the first 1000 Dow standards were published (*25*).

The more frequent types of errors are: (1) incorrect degree of hydration [pattern 240 is $CaSO_3.2H_2O$; pattern 338, $CoSO_4.H_2O$; pattern 623, $NiF_2.4H_2O$; pattern 864, $Na_2S.xH_2O$]; (2) chemical reaction between standard substance and water, oxygen, or carbon dioxide [pattern 193 is mixture of $CaCO_3$, $Ca(OH)_2$, and graphite (*7*); pattern 227, $Ca_{10}(OH)_2(PO_4)_6$ and $Ca(OH)_2$; pattern 215, vaterite plus calcite]; and (3) incorrect chemical formula [pattern 13 is $Al(OH)_3$, gibbsite; patterns 68 and 69 are largely $(Sb, As)_4O_6$; patterns 132 and 143 are largely $Bi(OH)_3$; pattern 269 refers to a mixture containing minor amount of hexamethylene tetramine]. Some errors in the diffraction data have been noted—e.g., the most intense line for $FeCl_2.2H_2O$ (pattern 409) is 5.5 Å. (40); the (020) reflection for Na_2SO_4III (pattern 859) should read 4.47 Å.

An examination of the useful compilation of powder data on minerals (*26*) reveals a similar state of affairs for these tabulated standards:

Pattern 3 (alabandite, MnS) lists in addition to the diffraction data for cubic manganese sulfide the lines 2.83 Å. and 1.995 Å. (probably NaCl). Pattern 23 [bravoite, $(Fe, Ni)S_2$] gives the accepted C2 pattern plus the noncubic reflections 3.08, 2.18, 2.04, 1.86, and 1.682 Å. Pattern 35 (chromite, $FeOCr_2O_3$) does not correspond to the $H1_1$ structure for $FeCr_2O_4$. Pattern 37 (clausthalite, PbSe) lists an extraneous 2.86 Å. reflection. In pattern 39 (coloradoite, HgTe) the strong (111) reflection is missing and the lines 2.82 Å. and 2.52 Å. appear extraneous, as does the line 2.79 Å. in pattern 95 (magnetite, Fe_3O_4). Pattern 93 (löllingite, $FeAs_2$) does not check the published data (*53*); the specimen used may have been an impure form of arsenopyrite. Pattern 137 (sphalerite, ZnS) checks the B3 structure except line 3.95 Å. Pattern 143 (sulvanite, Cu_3VS_4) omits the (220) reflection (1.90 Å.) and lists the extraneous lines 5.2, 4.15, 3.70, and 2.84 Å.

For a number of substances the innermost reflections have not been recorded: pattern 9 (argentite, Ag_2S) should include the line 3.91 Å. (*57*); pattern 16 (berthierite, $FeS.Sb_2S_3$), 8.0, 7.2, 5.7, 5.1 Å.; pattern 66 (gersdorffite, NiAsS), 3.99 Å.; pattern 76 (hauerite, MnS_2), 3.52 Å.; pattern 77 (hausmannite, Mn_3O_4), 4.92 Å.; pattern 95 (magnetite, Fe_3O_4), 4.85 Å.; pattern 141 (stibnite, Sb_2S_3), 8.2 Å. Pseudo-doublets due to absorption are noted in pattern 30 (cerargyrite, AgCl), the (200) reflection; and in pattern 38 (cobaltite, CoAsS), the (220) reflection.

While the experimental inaccuracies discussed can be remedied (the A.S.T.M. has an organization set up to issue new patterns periodically and correct old ones), there remain inherent limitations to the uniqueness of an established standard pattern. Solid solution, isomorphism, or structural similarity can contribute to the ambiguity of a standard pattern (see Tables V, VI, and VII). The absence of solid solution in an identified phase should always be checked by qualitative spectroscopic analysis and spot tests. If solid solution is indicated, a sensitive back-reflection technique is required to measure the *d*-shifts between standard and solid solution. Ambiguities attributed to isomorphism (see Tables V

and VI) or structural similarity (Table VII) usually are resolvable by spectroscopic analysis, spot tests, or some simple physical criterion such as solubility in water, melting point, etc. In the identification of multicomponent mixtures the intrinsic limitations illustrated in Tables V to VII become pronounced because of superposition of lines (see Tables II and XI).

The phases present in an unknown may be formed under rather haphazard or unequilibrated conditions conducive to the formation of defect structures (*6*, *27*, *51*, *52*). The differences between the diffraction pattern of such a defect structure and that of a normal standard may be subtle and escape the notice of the analyst. In general, structural irregularities in crystalline phases may be detected by changes in intensities of the diffraction lines (as compared to an ordered standard), by an increase of diffuse scattering, by the appearance of broad diffraction ghosts (*6*), by a broadening of one or more types of reflections, and by a change in the small angle scattering. Serious refinements in the normal powder technique, however, are required to gain information of sufficient reliability to justify an evaluation of the type of randomness in a particular phase. In a careful analysis of an unknown, due consideration should be given to the possible presence of defect structures (see Table VIII). The formation of a continuous range of solid solutions of cocrystallized salts is a rather common occurrence. Figure 2 illustrates the sensitivity of the back-reflection method for ascertaining this effect.

Table VII. Ambiguities Arising from Structural Similarities

d = interplanar spacing; I/I_1 = relative intensity

Substance												
Si	d, Å.	3.12	..	1.91	1.63	1.354	1.242	1.104	..	0.958	0.916	..
	I/I_1	1.00	..	1.00	0.63	0.18	0.25	0.40	..	0.06	0.13	..
β-ZnS	d, Å.	3.12	2.69	1.91	1.63	1.353	1.242	1.104	1.044	0.957	0.913	..
	I/I_1	1.00	0.05	0.75	0.50	0.05	0.18	0.15	0.05	0.03	0.04	..
CuCl	d, Å.	3.12	2.70	1.91	1.63	1.353	1.240	1.104	1.043	..	..	..
	I/I_1	1.00	0.08	0.60	0.30	0.06	0.08	0.06	0.04	..	..	..
CoO	d, Å.	..	2.45	2.12	1.50	1.281	1.227	1.060	0.975	0.951	0.869	0.819
	I/I_1	..	0.67	1.00	1.00	0.40	0.40	0.10	0.10	0.30	0.20	0.07
Cu_2O	d, Å.	3.00	2.45	2.12	1.51	1.283	1.228	1.065	0.977	0.953	0.869	0.819
	I/I_1	0.03	1.00	0.31	0.44	0.31	0.05	0.03	0.05	0.03	0.03	0.03
FeO	d, Å.	..	2.47	2.14	1.51	1.293	1.238	1.072	0.984	0.959	..	..
	I/I_1	..	0.50	1.00	0.63	0.15	0.08	0.03	0.03	0.05	..	..
CdO	d, Å.	2.70	2.34	1.65	1.412	1.352	1.171	1.075	..	..	..	..
	I/I_1	1.00	1.00	1.00	0.75	0.30	0.15	0.30	..	..	..	..
Ag_2O	d, Å.	2.72	2.36	1.67	1.422	1.360	1.179	1.082	..	..	..	..
	I/I_1	1.00	0.40	0.24	0.16	0.03	0.01	0.02	..	..	..	..
Al	d, Å.	2.33	2.02	1.43	1.219	1.168	..	..	..	..	..	..
	I/I_1	1.00	0.40	0.30	0.30	0.07	..	..	..	..	..	..
LiF	d, Å.	2.32	2.00	1.42	1.211	1.160	..	..	..	..	..	..
	I/I_1	0.67	1.00	0.23	0.03	0.03	..	..	..	..	..	..
α-Ce	d, Å.	2.97	2.57	1.815	1.55	1.481	1.288	1.179	..	..	..	..
	I/I_1	1.00	0.60	0.40	0.40	0.28	0.12	0.16	..	..	..	..
LiCl	d, Å.	2.96	2.56	1.81	1.55	1.482	1.283	1.178	..	..	..	..
	I/I_1	1.00	1.00	0.60	0.32	0.12	0.05	0.12	..	..	..	..
ThO_2	d, Å.	3.22	2.80	1.97	1.68	..	1.399	1.280	1.245	1.140	..	..
	I/I_1	1.00	0.38	0.75	0.88	..	0.13	0.38	0.25	0.38	..	..
Ca	d, Å.	3.21	2.80	1.97	1.68	1.61	..	1.28	1.246	1.138	..	..
	I/I_1	1.00	0.30	0.20	0.20	0.10	..	0.05	0.03	0.05	..	..
AgCl	d, Å.	3.20	2.77	1.96	1.67	1.60	1.385	1.270	1.240	1.131	..	..
	I/I_1	0.40	1.00	0.75	0.20	0.25	0.09	0.06	0.20	0.13	..	..

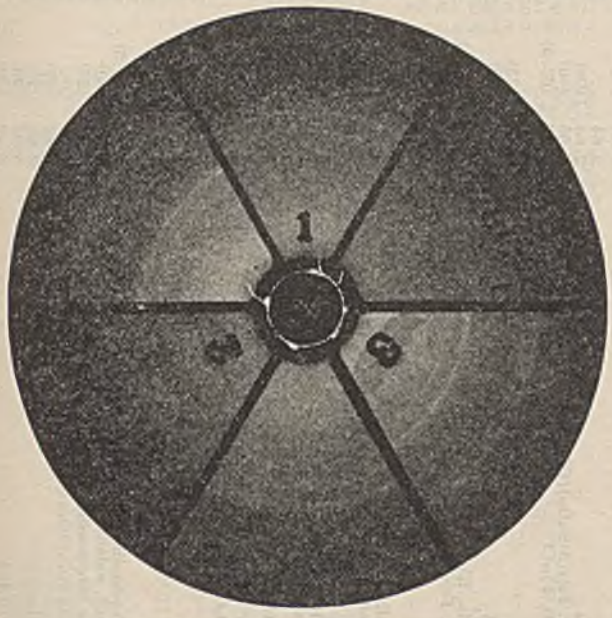

Figure 2. Back-Reflection Patterns

Taken with unfiltered FeK radiation. Specimen-to-film distance, 7.50 cm. Sector 1 refers to a mechanical mixture of 98% KI and 2% KBr; sector 2, same mixture crystallized from water; sector 3, same mixture fused. All samples ground to ~200-mesh powders

Classification of Standards. Up to the present about 2500 patterns have been cataloged at Dow. When one deals with this number of standards the identification of unknowns by the group classification system (*24*) is adequate, as has been amply demonstrated at Dow during the past ten years. However, it is of theoretical interest to consider what probable limitations may arise when a comparatively larger number of standards is considered. A statistical study of this problem has been made and is presented here purely as a guide to any modified index that might be considered by the diffraction analyst.

To arrive at a tentative answer to the above query it is instructive to examine how the three most intense diffraction lines (reference lines) for each of the cataloged patterns are distributed with respect to interplanar spacing. Figure 3 shows

Table VIII. Defect Structures

Examples	Diffraction Effects	References
Continuous range of solid solutions K(I, Br)	Merging of Kα doublet on back-reflections	...
Structures with "Leerstellen" $Fe_{1-x}R$ (R = O, S, Se, Te) Na_xWO_3	Occurrence of superstructure lines and anomalous change in lattice constants with x	(*20–23*)
$Mg_{1-x}Al_2O_{4-x}$	Broadening of diffraction lines	...
Pseudomorphism $Mg(OH)_{2(1-x)}O_x$	...	(*1*, *37*)
Randomness in layer structures $CdBr_2$ (Wechselstruktur)	X-ray data can be accounted for on basis of a unit of structure containing a fractional stoichiometric weight	(*3*, *27*, *28*, *36*, *38*, *39*, *45*)
Micas, clays $nCdCl_2mCd(OH)_2$, luster carbon	Broadening of diffraction lines, changes in intensities	(*27*, *28*, *38*)
Alloy systems with transition structures Al-Cu, Al-Ag, Cu_4FeNi_3, $AuCu_3$	Broad diffraction ghosts (*6*)	(*6*, *11*, *19*, *36*, *55*, *56*, *61*)

Table IX. Index to Aluminum-Containing Substances

Below headings 1, 2, 3 are listed respective reference lines and corresponding intensities for substances of second column. Pattern numbers refer to published Dow standards (*25*). Isomorphism is indicated by a bracket; corresponding structure (*16*) is stated in column "Pattern". Supplementary index (2, 1, 3, No.) refers to ordered arrangement of second reference line and is used whenever first reference line is obscured by superposition

No.	Substance	1 Å.		2 Å.		3 Å.		Pattern	Reference	2 Å.	1 Å.	3 Å.	No.	3 Å.	1 Å.	2 Å.	No.
1	$MnAl_2O_4$	1.398	(6)	2.49	(3)	2.39	(3)	556	...	1.151	1.99	2.82	7	1.423	2.47	2.38	24
2	$Na_2O.11Al_2O_3$	1.400	(75)	11.8	(40)	1.59	(40)	14	...	1.166	2.02	2.86	8	1.428	2.44	2.85	20
3	γ-Al_2O_3	1.40	(6B)	2.42	(2B)	2.01	(2B)	...	...	1.180	2.04	2.89	10	1.430	2.44	2.02	21
4	$NiAl_2O_4$	1.421	(8)	2.43	(6)	2.01	(6)	617	...	1.417	2.41	2.00	15	1.430	2.33	2.02	14
5	γ-AlO.OH, boehmite	1.86	(50)	3.17	(40)	6.15	(30)	...	(*18*)	1.423	2.43	2.85	18	1.431	2.44	2.85	19
6	Na_3AlF_6	1.94	(75)	2.75	(50)	1.57	(40)	813	...	1.455	2.48	1.58	26	1.434	2.48	2.24	25
7	AlNi	1.99	...	1.151	...	2.82	...	B2; 2.82 Å.	...	1.462	2.49	2.92	27	1.445	2.02	2.08	9
8	AlCo	2.02	...	1.166	...	2.86	...	B2; 2.856 Å.	...	1.52	2.64	3.73	32	1.481	10.1	4.48	78
9	$FeAl_3$	2.02	(75)	2.08	(62.5)	1.445	(15)	403	...	1.54	2.65	10.4	34	1.52	3.40	2.20	53
10	FeAl	2.04	(125)	1.180	(25)	2.89	(15)	402	...	1.54	2.58	2.88	29	1.54	2.42	2.84	16
11	α-Al_2O_3	2.08	(20)	1.59	(20)	2.55	(15)	11	...	1.55	2.59	2.89	30	1.55	2.68	1.90	37
12	Fe_3Al_8	2.11	(62.5)	2.05	(62.5)	3.20	(25)	404	...	1.58	2.65	2.96	33	1.57	1.94	2.75	6
13	LiAl	2.25	...	3.67	...	1.92	...	B32; 6.36 Å.	...	1.59	2.08	2.55	11	1.58	2.48	1.455	26
14	Al	2.33	(100)	2.02	(40)	1.430	(30)	1	...	1.62	2.71	3.03	39	1.59	1.400	11.8	2
15	$MgAl_2O_4$	2.41	(100)	1.417	(75)	2.00	(62.5)	497	...	1.64	3.10	2.95	43	1.63	3.99	2.31	66
16	$CaAl_2$	2.42	(125)	2.84	(50)	1.54	(40)	C15; 8.02 Å.	...	1.76	3.52	2.11	59	1.64	3.13	1.92	44
17	$CeAl_2$	2.42	...	2.84	...	2.32	...	C15; 8.04 Å.	...	1.84	2.60	3.67	31	1.66	2.87	2.80	42
18	$CuAl_2O_4$	2.43	(15)	1.423	(10)	2.85	(5)	343	...	1.89	2.67	3.78	36	1.70	3.25	1.99	48
19	$ZnAl_2O_4$	2.44	(15)	2.85	(8)	1.431	(6)	962	...	1.90	2.68	1.55	37	1.78	3.41	2.09	54
20	$CoAl_2O_4$	2.44	(50)	2.85	(25)	1.428	(25)	$H1_1$; 8.08 Å.	...	1.92	3.13	1.64	44	1.81	3.46	2.12	56
21	$FeAl_2O_4$	2.44	(25)	2.02	(20)	1.430	(20)	$H1_1$; 8.10 Å.	...	1.99	3.25	1.70	48	1.85	3.53	2.16	60
22	$LaAl_3$	2.46	...	2.89	...	2.36	...	C15; 8.16 Å.	...	2.02	2.33	1.430	14	1.86	3.22	2.82	47
23	Al_2Cl_6	2.46	(62.5)	5.8	(40)	2.80	(40)	4	...	2.02	2.44	1.430	21	1.92	2.25	3.67	13
24	Mg_3Al_8	2.47	(75)	2.38	(40)	1.423	(30)	495	...	2.05	2.11	3.20	12	2.00	2.41	1.417	15
25	Mg_2Al_3	2.48	(150)	2.24	(50)	1.434	(50)	496	...	2.08	2.02	1.445	9	2.01	1.40	2.42	3
26	$FeO.Cr_2O_3.Al_2O_3$	2.48	(50)	1.455	(20)	1.58	(17.5)	427	...	2.09	3.41	1.78	54	2.01	1.421	2.43	4
27	$MnAl_2O_4$	2.49	...	1.462	...	2.92	...	$H1_1$; 8.27 Å.	...	2.09	3.62	6.27	62	2.05	3.29	2.30	51
28	$KAl_2(AlSi_3O_{10})(OH)_2$, muscovite	2.56	(15)	9.99	(9)	4.47	(8)	16	(*16, 50*)	2.12	3.46	1.81	56	2.11	3.52	1.76	59
29	$(Fe, Mg)_2Al_2(SiO_4)_3$	2.58	(100)	1.54	(62.5)	2.88	(50)	$S1_4$; 11.51 Å.	...	2.16	3.53	1.85	60	2.12	3.68	2.61	63
30	$Mn_3Al_2(SiO_4)_3$	2.59	(100)	1.55	(40)	2.89	(30)	$S1_4$; 11.60 Å.	...	2.20	3.40	1.52	53	2.14	3.50	3.08	57
31	$YAlO_3$	2.60	...	1.84	...	3.67	...	$E2_1$; 3.67 Å.	...	2.23	5.14	2.57	76	2.15	3.72	2.63	64
32	AlNd	2.64	...	1.52	...	3.73	...	B2; 3.73 Å.	...	2.24	2.48	1.434	25	2.31	4.36	7.46	73
33	$Ca_3Al_2(SiO_4)_3$	2.65	(100)	1.58	(62.5)	2.96	(40)	$S1_4$; 11.87 Å.	...	2.30	3.29	2.05	51	2.32	2.42	2.84	17
34	$(K, Na)(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$, biotite-phlogopite	2.65	(40)	1.54	(25)	10.4	(15)	...	(*46, 50*)	2.31	3.99	1.63	66	2.36	2.46	2.89	22
35	$Al_{13}Si_5O_{20}(OH, F)_{18}Cl$	2.66	(62.5)	7.98	(40)	4.17	(40)	SO_8; 13.82 Å.	...	2.38	2.47	1.423	24	2.36	4.05	3.01	67
36	$LaAlO_3$	2.67	...	1.89	...	3.78	...	$E2_1$; 3.78 Å.	...	2.42	1.40	2.01	3	2.39	1.398	2.49	1
37	$3CaO.Al_2O_3$	2.68	(25)	1.90	(6)	1.55	(6)	170	...	2.43	1.421	2.01	4	2.44	2.68	4.92	38
38	$5CaO.3Al_2O_3$	2.68	(30)	4.92	(20)	2.44	(15)	171	...	2.49	1.398	2.39	1	2.45	4.88	4.39	75
39	$(Na, Li)_3AlF_6$	2.71	...	1.62	...	3.03	...	$S1_4$; 12.10 Å.	...	2.61	3.68	2.12	63	2.48	4.42	3.95	74
40	$(OH)_2(Ca, Na, K)_{2-3}(Mg, Fe, Al)_5(Si, Al)_8O_{22}$, hornblende	2.73	(17.5)	8.7	(15)	3.12	(8)	...	(*46*)	2.63	3.72	2.15	64	2.51	2.75	3.08	41
41	$(Na, Al, Ca, Fe)_3Mn_2(PO_4)_{2.5}(OH)_2$, griphite	2.75	(50)	3.08	(8)	2.51	(8)	...	(*44*)	2.75	1.94	1.57	6	2.52	3.20	4.05	46
42	Al_4C_3	2.87	(25)	2.80	(25)	1.66	(25)	3	...	2.80	2.87	1.66	42	2.54	15.2	4.45	80
43	$NaAlCl_4$	3.10	(17.5)	1.64	(17.5)	2.95	(15)	6	...	2.80	4.32	5.46	70	2.55	2.08	1.59	11
44	AlP	3.13	...	1.92	...	1.64	...	B3; 5.43 Å.	...	2.81	4.34	3.28	71	2.57	5.14	2.23	76
45	$NaAlSi_3O_8$, albite	3.20	(50)	4.05	(17.5)	3.66	(12.5)	854	...	2.82	3.22	1.86	47	2.65	3.50	5.8	58
46	$CaAl_2Si_2O_8$, anorthite	3.20	(50)	4.05	(15)	2.52	(10)	...	(*46*)	2.83	4.35	5.5	72	2.80	2.46	5.8	23
47	Al_2S_3	3.22	(30)	2.82	(25)	1.86	(20)	24	...	2.84	2.42	1.54	16	2.82	1.99	1.151	7
48	AlAs	3.25	...	1.99	...	1.70	...	B3; 5.63 Å.	...	2.84	2.42	2.32	17	2.85	2.43	1.423	18
49	$KAlSi_3O_8$, microcline	3.25	(40)	4.23	(15)	3.35	(10)	703	...	2.85	2.44	1.428	20	2.86	2.02	1.166	8
50	$NH_4Al(SO_4)_2.12H_2O$	3.26	(50)	4.30	(40)	5.4	(30)	21	...	2.85	2.44	1.431	19	2.88	2.58	1.54	29
51	$AlCl_3.6H_2O$	3.29	(75)	2.30	(40)	2.05	(40)	5	...	2.89	2.46	2.36	22	2.89	2.59	1.55	30
52	$(NH_3CH_3)Al(SO_4)_2.12H_2O$	3.32	...	4.40	...	5.56	...	$H4_{13}$; 12.44 Å.	...	3.01	4.05	2.36	67	2.89	2.04	1.180	10
53	Al_2SiO_5	3.40	(50)	2.20	(30)	1.52	(30)	15	...	3.08	3.50	2.14	57	2.92	2.49	1.462	27
54	$PtAl_2$	3.41	...	2.09	...	1.78	...	C1; 5.91 Å.	...	3.08	2.75	2.51	41	2.93	3.42	5.6	55
55	$NaAlSi_2O_6.H_2O$, analcite	3.42	(75)	5.6	(40)	2.93	(40)	$S6_1$; 13.68 Å.	...	3.17	1.86	6.15	5	2.95	3.10	1.64	43
56	$AuAl_2$	3.46	...	2.12	...	1.81	...	C1; 5.99 Å.	...	3.59	3.84	3.38	65	2.96	2.65	1.58	33
57	AlI_3	3.50	(40)	3.08	(20)	2.14	(20)	9	...	3.65	4.23	3.98	68	3.03	2.71	1.62	39
58	$Al_2(SO_4)_3$	3.50	(50)	5.8	(15)	2.65	(15)	19	...	3.67	2.25	1.92	13	3.12	2.73	8.7	40
59	AlF_3	3.52	(15)	1.76	(2)	2.11	(1.5)	8	...	3.86	5.50	3.28	77	3.14	12.2	4.48	79
60	AlSb	3.53	...	2.16	...	1.85	...	B3; 6.12 Å.	...	3.95	4.42	2.48	74	3.20	2.11	2.05	12
61	$Al_2Si_2O_5(OH)_4$, kaolin	3.58	(12.5)	7.2	(10)	4.43	(10)	17	(*15, 50*)	4.03	4.29	3.24	69	3.24	4.29	4.03	69
62	$Na_4(AlSiO_4)_3Cl$, sodalite	3.62	(150)	2.09	(50)	6.27	(25)	$S6_2$; 8.87 Å.	...	4.05	3.20	3.66	45	3.28	4.34	2.81	71
63	$Na_8(AlSiO_4)_6.SO_4$, noselite	3.68	(25)	2.61	(12.5)	2.12	(12.5)	$S6_2$; 9.03 Å.	...	4.05	3.20	2.52	46	3.28	5.50	3.86	77
64	$(Na, Ca)_{4-3}(AlSiO_4)_3(SO_4)_{1-2}$, haüynite	3.72	...	2.63	...	2.15	...	$S6_2$; 9.11 Å.	...	4.23	3.25	3.35	49	3.35	3.25	4.23	49
65	$AlBr_3.6H_2O$	3.84	(7)	3.59	(6)	3.38	(6)	2	...	4.30	3.26	5.4	50	3.38	3.84	3.59	65
66	α-AlO.OH, diaspore	3.99	(75)	2.31	(75)	1.63	(62.5)	12	...	4.39	4.88	2.45	75	3.66	3.20	4.05	45
67	$Al(NO_3)_3.9H_2O$	4.05	(20)	3.01	(15)	2.36	(15)	10	...	4.40	3.32	5.56	52	3.67	2.60	1.84	31
68	$NaAl(SO_4)_2.12H_2O$	4.23	(50)	3.65	(25)	3.98	(20)	23	...	4.45	15.2	2.54	80	3.73	2.64	1.52	32
69	$KAl(SO_4)_2.12H_2O$	4.29	(50)	4.03	(20)	3.24	(20)	22	...	4.48	10.1	1.481	78	3.78	2.67	1.89	36
70	$TlAl(SO_4)_2.12H_2O$	4.32	...	2.80	...	5.46	...	$H4_{13}$; 12.21 Å.	...	4.48	12.2	3.14	79	3.98	4.23	3.65	68
71	$RbAl(SO_4)_2.12H_2O$	4.34	(30)	2.81	(20)	3.28	(15)	738	...	4.92	2.68	2.44	38	4.17	2.66	7.98	35
72	$CsAl(SO_4)_2.12H_2O$	4.35	(40)	2.83	(30)	5.5	(15)	302	...	5.6	3.42	2.93	55	4.43	3.58	7.2	61
73	$(OH)_4Si_2Al_2O_5$, metahalloysite	4.36	...	7.46	...	2.31	...	...	(*46*)	5.8	2.46	2.80	23	4.47	2.56	9.99	28
74	$Al_2(SO_4)_3.18H_2O$	4.42	(50)	3.95	(30)	2.48	(20)	20	...	5.8	3.50	2.65	58	5.4	3.26	4.30	50
75	$Al_2O_3.3H_2O$, gibbsite	4.88	(125)	4.39	(62.5)	2.45	(40)	13	...	7.2	3.58	4.43	61	5.46	4.32	2.80	70
76	$(NH_4)_3AlF_6$	5.14	...	2.23	...	2.57	...	$J2_1$; 8.90 Å.	...	7.46	4.36	2.31	73	5.5	4.35	2.83	72
77	$AlF_3.3^1/_2H_2O$	5.50	(50)	3.86	(25)	3.28	(25)	7	...	7.98	2.66	4.17	35	5.56	3.32	4.40	52
78	$(OH)_4SiAl_2O_5.2H_2O$, halloysite	10.1	...	4.48	...	1.481	...	...	(*46*)	8.7	2.73	3.12	40	6.15	1.86	3.17	5
79	Bentonite	12.2	(40)	4.48	(20)	3.14	(8)	18	...	9.99	2.56	4.47	28	6.27	3.62	2.09	62
80	$(OH)_2Al_2Si_4O_{10}.nH_2O$, montmorillonite	15.2	...	4.45	...	2.54	...	...	(*46*)	11.8	1.400	1.59	2	10.4	2.65	1.54	34

Table X. Index to Iron-Containing Substances

Below headings 1, 2, 3 are listed respective reference lines and corresponding intensities for substances of second column. Pattern numbers without parenthetical designation refer to published Dow standards (*25*) Isomorphism is indicated by a bracket; corresponding structure (*16*) is stated in column "Pattern". Supplementary index (2, 1, 3, No.) refers to ordered arrangement of second reference line and is used whenever first reference line is obscured by superposition.

No.	Substance	1 Å.		2 Å.		3 Å.		Pattern	Reference	2 Å.	1 Å.	3 Å.	No.	3 Å.	1 Å.	2 Å.	No.
1	FeS_2, pyrite	1.63	(62.5)	2.70	(50)	2.42	(30)	443	...	1.166	2.01	1.428	7	1.136	2.18	1.88	20
2	$(Fe, Ni)S_2$	1.675	...	2.77	...	2.49	...	23 (*26*)	...	1.180	2.04	2.89	9	1.193	2.00	1.82	6
3	$(Fe, Ni)_9S_8$	1.77	...	3.03	...	1.95	...	110 (*26*)	...	1.184	2.05	1.450	11	1.273	2.08	1.80	15
4	$FeSi_2$	1.84	(100)	2.37	(62.5)	5.1	(30)	433	...	1.196	2.07	1.465	13	1.283	2.10	1.82	17
5	Cu_5FeS_4	1.93	...	3.30	...	3.15	...	20 (*26*), 29 (*60*)	...	1.432	2.44	2.02	24	1.42	2.71	1.66	48
6	FeSi	2.00	(100)	1.82	(40)	1.193	(20)	432	...	1.455	2.48	1.58	26	1.428	2.01	1.166	7
7	α-Fe	2.01	(40)	1.166	(15)	1.428	(6)	401	...	1.464	2.07	2.39	14	1.445	2.02	2.08	8
8	$FeAl_3$	2.02	(75)	2.08	(62.5)	1.445	(15)	403	...	1.468	2.50	1.60	27	1.450	2.05	1.184	11
9	FeAl	2.04	(125)	1.180	(25)	2.89	(15)	402	...	1.476	2.51	2.95	29	1.465	2.07	1.196	13
10	$Fe_{1-x}S$	2.04	(100)	1.71	(50)	2.97	(40)	B8 $\begin{cases} a = 3.43 \text{ Å.} \\ c = 5.68 \end{cases}$	...	1.476	2.52	1.61	30	1.54	2.96	1.81	60
11	β-Fe(1070° K.)	2.05	...	1.184	...	1.450	...	A2; 2.90 Å.	...	1.481	2.53	1.61	31	1.541	2.95	1.81	59
12	FeS	2.06	(75)	2.97	(25)	2.65	(25)	442	...	1.483	2.53	1.61	33	1.58	2.48	1.455	26
13	δ-Fe(1700° K.)	2.07	...	1.196	...	1.465	...	A2; 2.93 Å.	...	1.484	2.53	2.97	32	1.59	3.03	1.86	64
14	$(63Li_2Fe_2O_4.37Li_2TiO_3)$	2.07	...	1.464	...	2.39	...	(B1); 4.142 Å.	...	1.488	2.54	1.62	34	1.60	2.50	1.468	27
15	Taenite, 57.7% Fe, 40.8% Ni, 0.5% P	2.08	...	1.80	...	1.273	...	A1; 3.60 Å.	...	1.49	2.55	1.62	37	1.601	3.07	1.88	65
16	Fe_3N	2.09	(40)	2.19	(10)	1.61	(10)	417	...	1.492	2.54	1.63	35	1.61	2.09	2.19	16
17	γ-Fe(1370° K.)	2.10	...	1.82	...	1.283	...	A1; 3.63 Å.	...	1.497	2.55	1.63	36	1.61	2.52	1.476	30
18	Fe_2Al_5	2.11	(62.5)	2.05	(62.5)	3.20	(25)	404	...	1.51	2.14	2.47	19	1.61	2.53	1.481	31
19	FeO	2.14	(40)	1.51	(25)	2.47	(20)	425	...	1.51	2.57	1.64	38	1.61	2.53	1.483	33
20	Fe_4N	2.18	(10)	1.88	(4)	1.136	(3)	418	...	1.54	2.57	2.88	39	1.62	2.54	1.488	34
21	Fe_2P	2.23	(17.5)	2.03	(10)	1.92	(10)	429	...	1.54	2.58	2.88	40	1.62	2.55	1.49	37
22	FeAsS	2.43	(30)	1.82	(17.5)	2.82	(8)	12 (*26*)	...	1.54	2.65	10.4	43	1.63	2.54	1.492	35
23	$(FeAs_2)$	2.43	...	2.67	...	1.81	...	93 (*26*)	...	1.59	2.66	2.97	44	1.63	2.55	1.497	36
24	$FeAl_2O_4$	2.44	(25)	1.432	(20)	2.02	(20)	$H1_1$; 8.10 A.	...	1.61	2.70	3.00	47	1.63B	3.11	1.91	66
25	(Co, Fe)AsS	2.45	...	2.72	...	1.82	...	67 (*26*)	...	1.66	2.71	1.42	48	1.64	2.57	1.51	38
26	$FeO.Cr_2O_3.Al_2O_3$	2.48	(50)	1.455	(20)	1.58	(17.5)	427	...	1.678	2.86	2.37	55	1.67	2.62	3.08	42
27	$FeCr_2O_4$	2.50	(62.5)	1.468	(62.5)	1.60	(50)	$H1_1$; 8.33 Å.	...	1.71	2.04	2.97	10	1.71	2.94	4.71	58
28	$Cu_2Fe_2O_4$	2.50	...	2.84	...	2.23	...	51 (*26*); 47 (*60*)	...	1.76	2.71	3.45	49	1.72	2.73	2.53	50
29	$MgFe_2O_4$	2.51	(75)	1.476	(30)	2.95	(20)	527	...	1.77	3.02	2.50	63	1.72	2.99	3.65	62
30	$NiFe_2O_4$	2.52	...	1.476	...	1.61	...	$H1_1$; 8.35 Å.	...	1.80	2.08	1.273	15	1.75	3.22	1.88	67
31	$CoFe_2O_4$	2.53	(50)	1.481	(40)	1.61	(25)	$H1_1$; 8.38 Å.	...	1.81	2.95	1.541	59	1.81	2.43	2.67	23
32	$ZnFe_2O_4$	2.53	(50)	1.484	(15)	2.97	(12.5)	979	...	1.81	2.96	1.54	60	1.82	2.45	2.72	25
33	$FeFe_2O_4$	2.53	(62.5)	1.483	(50)	1.61	(40)	426	...	1.82	2.00	1.193	6	1.84	2.69	2.51	46
34	(Mn, Mg)Fe_2O_4	2.54	...	1.488	...	1.62	...	$H1_1$; 8.42 Å.	...	1.82	2.10	1.283	17	1.92	2.23	2.03	21
35	$CuFe_2O_4$	2.54	...	1.492	...	1.63	...	$H1_1$; 8.44 Å.	...	1.82	2.43	2.82	22	1.95	1.77	3.03	3
36	FeV_2O_4	2.55	...	1.497	...	1.63	...	$H1_1$; 8.47	...	1.86	3.03	1.59	64	1.982	2.81	3.97	54
37	(Fe, Zn, Mn)(Fe, Mn)$_2O_4$	2.55	...	1.49	...	1.62	...	60 (*26*)	...	1.88	2.18	1.136	20	1.99	3.25	4.78	68
38	$MnFe_2O_4$	2.57	...	1.51	...	1.64	...	$H1_1$; 8.54	...	1.88	3.07	1.601	65	2.02	2.44	1.432	24
39	$Fe_2Al_2(SiO_4)_3$	2.57	(100)	1.54	(40)	2.88	(30)	$S1_4$; 11.51 Å.	...	1.88	3.22	1.75	67	2.06	3.63	2.57	73
40	(Mg, Fe)$_2Al_2(SiO_4)_3$	2.58	(100)	1.54	(62.5)	2.88	(50)	$S1_4$; 11.51 Å.	...	1.91	3.11	1.63B	66	2.09	2.92	2.22	57
40.5	$Fe_{1-x}As_{2-x}$	2.59	...	2.32	...	2.52	...	...	(*53*)	1.94	2.75	5.7	53	2.18	2.917	2.46	56
41	$FeS.Sb_2S_3$	2.60	...	3.62	...	3.15	...	16 (*26*)	...	2.03	2.23	1.92	21	2.18	6.9	3.61	112
42	$CdFe_2O_4$	2.62	(30)	3.08	(17.5)	1.67	(12.5)	161	...	2.04	7.4	3.51	115	2.23	2.50	2.84	28
43	$(K, Na)(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$, biotite-phlogopite	2.65	(40)	1.54	(25)	10.4	(15)	...	(*46, 50*)	2.05	2.11	3.20	18	2.37	2.86	1.678	55
44	$Ca_3(Al, Fe)_2(SiO_4)_3$	2.66	(100)	1.59	(62.5)	2.97	(40)	$S1_4$; 11.89 Å.	...	2.08	2.02	1.445	8	2.39	2.07	1.464	14
45	Fe_2Cl_6	2.68	(62.5)	2.08	(25)	5.9	(20)	407	...	2.08	2.68	5.9	45	2.42	1.63	2.70	1
46	Fe_2O_3	2.69	(40)	2.51	(30)	1.84	(25)	423	...	2.19	2.09	1.61	16	2.47	2.14	1.51	19
47	$Ca_3Fe_2(SiO_4)_3$	2.70	...	1.61	...	3.00	...	$S1_4$; 12.02 Å.	...	2.22	2.92	2.09	57	2.47	6.35	3.30	107

(*Continued on page 216*)

Table X (Cont.)

No.	Substance	1 Å.		2 Å.		3 Å.		Pattern	Reference	2 Å.	1 Å.	3 Å.	No.	3 Å.	1 Å.	2 Å.	No.
48	$(Mn, Fe)_2O_3$	2.71	(62.5)	1.66	(30)	1.42	(15)	D5₃; 9.37 Å.	...	2.22	5.13	2.57	91	2.49	1.675	2.77	2
49	FeS_2, marcasite	2.71	(100)	1.76	(62.5)	3.45	(40)	96 (*26*)	...	2.28	5.25	2.63	92	2.50	3.02	1.77	63
50	$FeTiO_3$	2.73	(50)	2.53	(40)	1.72	(25)	81 (*26*)	...	2.32	5.35	2.68	93	2.50	5.0	3.55	88
51	$(OH)_2(Ca, Na, K)_{2-3}(Mg, Fe, Al)_5(Si, Al)_8O_{22}$, hornblende	2.73	(17.5)	8.7	(15)	3.12	(8)	...	(*46*)	2.32	2.59	2.52	40.5	2.51	2.75	3.08	52
52	$(Na, Al, Ca, Fe)_3Mn_3(PO_4)_{2.5}(OH)_3$, griphite	2.75	(50)	3.08	(8)	2.51	(8)	...	(*44*)	2.37	1.84	5.1	4	2.51	4.35	3.10	80.8
53	$Na_4Fe(CN)_6$	2.75	(100)	1.94	(40)	5.7	(12.5)	809	...	2.45	4.21	2.70	79	2.52	2.59	2.32	40.5
53.2	$FePO_4.2H_2O$, phosphosiderite	2.77	(100)	4.33	(62.5)	4.67	(40)	...	(*42*)	2.46	2.917	2.18	56	2.57	5.13	2.22	91
54	Na_3FeF_6	2.81	(62.5)	3.97	(50)	1.982	(50)	Cryolite; 813	...	2.48	5.73	2.87	100	2.61	4.75	2.98	85
55	$(Ni, Fe)_3S_4$	2.86	...	1.678	...	2.37	...	156 (*26*)	...	2.51	2.69	1.84	46	2.62	6.6	4.10	109
56	$(Fe, Mn)WO_4$	2.917	...	2.46	...	2.18	...	162 (*26*)	...	2.53	2.73	1.72	50	2.63	5.25	2.28	92
57	$K_4Fe(CN)_6.3H_2O$	2.92	(100)	2.22	(30)	2.09	(20)	671	...	2.54	5.86	5.08	101	2.65	2.06	2.97	12
58	$FeWO_4$	2.94	(40)	4.71	(10)	1.71	(17.5)	58 (*26*)	...	2.55	3.33	7.4	69	2.68	5.35	2.32	93
59	$5Cu_2S.2(Cu, Fe, Zn)S.2As_2S_3$	2.95	...	1.81	...	1.541	...	147 (*26*)	...	2.55	5.1	3.60	89	2.70	4.21	2.45	79
60	$5Cu_2S.2(Cu, Fe, Zn)S.2Sb_2S_3$	2.96	...	1.81	...	1.54	...	150 (*26*)	...	2.57	3.63	2.06	73	2.72	3.40	2.81	70
61	$K_4Fe(CN)_6$	2.98	(30)	3.60	(25)	2.84	(25)	670	...	2.57	3.64	5.1	74	2.76	5.7	3.44	99
62	$(Fe, Mn)(Cb, Ta)_2O_6$	2.99	(30)	3.65	(8)	1.72	(8)	40 (*26*)	...	2.62	4.83	5.1	86	2.76	6.0	3.14	102
63	$FeCr_2S_4$	3.02	...	1.77	...	2.50	...	50 (*26*)	...	2.62	6.04	5.24	103	2.79	4.25	3.25	80
64	$CuFeS_2$	3.03	(30)	1.86	(25)	1.59	(6)	384; 32 (*26*), 42 (*60*)	...	2.63	6.07	5.26	104	2.82	2.43	1.82	22
65	$(Cu, Fe, Mo, Sn)_4(S, As, Te)_{3-4}$	3.07	...	1.88	...	1.601	...	41 (*26*)	...	2.67	2.43	1.81	23	2.84	2.98	3.60	61
66	$Cu_2S.FeS.SnS_2$	3.11	...	1.91	...	1.63B	...	138 (*26*)	...	2.70	1.63	2.42	1	2.87	5.73	2.48	100
67	$CuS.2FeS$	3.22	...	1.88	...	1.75	...	46 (*26*)	...	2.72	2.45	1.82	25	2.88	2.57	1.54	39
68	$FeSO_4$	3.25	(62.5)	4.78	(15)	1.99	(12.5)	435	...	2.74	6.33	5.49	106	2.88	2.58	1.54	40
69	β-FeO.OH	3.33	(20)	2.55	(15)	7.4	(12.5)	...	(*9*)	2.75	5.5	4.28	95	2.89	2.04	1.180	9
70	$4PbS.FeS.3Sb_2S_3$	3.40	...	2.81	...	2.72	...	82 (*26*)	...	2.77	1.675	2.49	2	2.89	4.75	4.16	84
71	$FeSO_4.H_2O$	3.42	(40)	4.85	(20)	3.13	(15)	436	...	2.81	3.40	2.72	70	2.94	4.14	3.09	77
72	$Fe_2(SO_4)_3.H_2O$	3.53	(10)	6.8	(8)	4.75	(8)	434	...	2.82	5.7	4.95	98	2.95	2.51	1.476	29
73	$K_2CuFe(CN)_6$	3.63	(40)	2.57	(30)	2.06	(25)	363	...	2.83	6.55	5.67	108	2.97	2.04	1.71	10
74	$CaK_2Fe(CN)_6$	3.64	(30)	2.57	(12.5)	5.1	(9)	196	...	2.84	2.50	2.23	28	2.97	2.53	1.484	32
75	$Zn_2Fe(CN)_6.3H_2O$	4.08	(20)	5.4	(17.5)	3.64	(8)	971	...	2.89	6.66	5.77	110	2.97	2.66	1.59	44
76	$Pb_2Fe(CN)_6.3H_2O$	4.10	(15)	3.67	(15)	6.3	(10)	455	...	2.97	2.06	2.65	12	3.00	2.70	1.61	47
77	$K_3Fe(CN)_6$	4.14	(62.5)	3.09	(30)	2.94	(30)	669	...	2.98	4.75	2.61	85	3.00	5.4	3.98	94
78	$FeSO_4(NH_4)_2SO_4.6H_2O$	4.20	(30)	3.80	(20)	3.03	(17.5)	441	...	3.03	1.77	1.95	3	3.03	4.20	3.80	78
79	α-FeO(OH), goethite	4.21	(25)	2.45	(20)	2.70	(9)	424	(*9, 54*)	3.08	2.62	1.67	42	3.12	2.73	8.7	51
80	$AgFe_2S_{3-4}$	4.25	...	3.25	...	2.79	...	140 (*26*)	...	3.08	2.75	2.51	52	3.13	3.42	4.85	71
80.8	$FePO_4.2H_2O$, strengite	4.35	(40)	3.10	(25)	2.51	(25)	...	(*43*)	3.09	4.14	2.94	77	3.15	1.93	3.30	5
81	$FeNH_4(SO_4)_2.12H_2O$	4.37	(50)	7.1	(40)	3.73	(40)	440	...	3.10	4.35	2.51	80.8	3.15	2.60	3.62	41
82	$FeC_4H_4O_6$	4.44	(20)	3.51	(17.5)	5.8	(15)	444	...	3.14	6.0	2.76	102	3.19	7.0	3.62	113
83	$Fe(C_6H_4OHSO_3)_2$	4.59	(40)	5.6	(15)	4.20	(15)	428	...	3.25	4.25	2.79	80	3.20	2.11	2.05	18
84	$Na_2Fe(CN)_5NO.2H_2O$	4.75	(20)	4.16	(20)	2.89	(20)	811	...	3.30	1.93	3.15	5	3.23	4.90	3.78	87
85	$FeC_2O_4.2H_2O$	4.75	(17.5)	2.98	(6)	2.61	(6)	419	...	3.30	6.35	2.47	107	3.45	2.71	1.76	49
86	$2Na_3Fe(C_2O_4)_3.9H_2O$	4.83	(25)	2.62	(20)	5.1	(15)	422	...	3.44	5.7	2.76	99	3.48	5.5	3.91	96
87	$FeSO_4.7H_2O$	4.90	(62.5)	3.78	(40)	3.23	(12.5)	438	...	3.51	4.44	5.8	82	3.51	7.4	2.04	115
88	$Cu_2Fe(CN)_6.7H_2O$	5.0	(40)	3.55	(30)	2.50	(20)	362	...	3.51	9.8	5.1	117	3.60	5.1	2.55	89
89	$Fe_4[Fe(CN)_6]_3$	5.1	(62.5)	2.55	(30)	3.60	(20)	412	...	3.55	5.0	2.50	88	3.64	4.08	5.4	75
90	$Ca_2Fe(CN)_6.12H_2O$	5.1	(30)	5.5	(15)	4.70	(12.5)	195	...	3.60	2.98	2.84	61	3.70	6.7	3.99	111
91	Li_3FeF_6	5.13	...	2.22	...	2.57	...	($J2_1$); 8.88 Å.	...	3.61	6.9	2.18	112	3.73	4.37	7.1	81
92	$(NH_4)_3FeF_6$	5.25	...	2.28	...	2.63	...	$J2_1$; 9.10 Å.	...	3.62	2.60	3.15	41	3.99	5.5	4.49	97
93	Na_3FeF_6	5.35	...	2.32	...	2.68	...	($J2_1$); 9.26 Å.	...	3.62	7.0	3.19	113	4.20	4.50	5.6	83
94	$FeCl_2.4H_2O$	5.4	(40)	3.98	(40)	3.00	(40)	410	...	3.65	2.99	1.72	62	4.28	5.5	2.75	95
95	$FeCl_2.2H_2O$	5.5	(40)	2.75	(30)	4.28	(25)	409	...	3.67	4.10	6.3	76	4.50	9.5	5.2	116
96	$FeF_2.4^1/_2H_2O$	5.5	(50)	3.91	(25)	3.48	(20)	413	...	3.78	4.90	3.23	87	4.67	2.77	4.33	53.2
97	$FeSO_4.4H_2O$	5.5	(40)	4.49	(40)	3.99	(30)	437	...	3.80	4.20	3.03	78	4.70	5.1	5.5	90
98	Iron ammonium chloride	5.7	(17.5)	2.82	(17.5)	4.95	(12.5)	411	...	3.91	5.5	3.48	96	4.75	3.53	6.8	72
99	$Fe(H_2PO_2)_2$	5.7	(50)	3.44	(10)	2.76	(6)	430	...	3.97	2.81	1.982	54	4.95	5.7	2.82	98
100	K_2FeF_6	5.73	...	2.48	...	2.87	...	($J2_1$); 9.93 Å.	...	3.98	5.4	3.00	94	5.08	5.86	2.54	101
101	$Fe(NH_3)_6Cl_2$	5.86	...	2.54	...	5.08	...	$J1_1$; 10.15 Å.	...	3.99	6.7	3.70	111	5.1	1.84	2.37	4
102	$FeCl_2.6H_2O$	6.0	(40)	3.14	(30)	2.76	(20)	408	...	4.10	6.6	2.62	109	5.1	3.64	2.57	74
103	$Fe(NH_3)_6Br_2$	6.04	...	2.62	...	5.24	...	$J1_1$; 10.47 Å.	...	4.16	4.75	2.89	84	5.1	4.83	2.62	86
104	$Fe(NH_3)_6(ClO_4)_2$	6.07	...	2.63	...	5.26	...	$J1_1$; 10.52 Å.	...	4.33	2.77	4.67	53.2	5.1	9.8	3.51	117
105	$Fe(HCO_2)_2.H_2O$	6.2	(8)	8.4	(5)	7.6	(3)	414	...	4.49	5.5	3.99	97	5.7	2.75	1.94	53
106	$Fe(NH_3)_6I_2$	6.33	...	2.74	...	5.49	...	$J1_1$; 10.97 Å.	...	4.71	2.94	1.71	58	5.8	4.44	3.51	82
107	γ-FeO.OH	6.35	(62.5)	3.30	(62.5)	2.47	(62.5)	...	(*9, 54*)	4.78	3.25	1.99	68	5.9	2.68	2.08	45
108	$Fe(NH_3)_6(BF_4)_2$	6.55	...	2.83	...	5.67	...	$J1_1$; 11.34 Å.	...	4.85	3.42	3.13	71	5.24	6.04	2.62	103
109	$Fe(NO_3)_3.9H_2O$	6.6	(25)	4.10	(25)	2.62	(25)	416	...	5.1	10.0	7.7	118	5.26	6.07	2.63	104
110	$Fe(NH_3)_6(SO_3F)_2$	6.66	...	2.89	...	5.77	...	$J1_1$; 11.54 Å.	...	5.2	9.5	4.50	116	5.49	6.33	2.74	106
111	$Fe(AsO_4)_2.6H_2O$	6.7	(5)	3.99	(2)	3.70	(2)	405	...	5.4	4.08	3.64	75	5.67	6.55	2.83	108
112	$K_3Fe(C_2O_4)_3.3H_2O$	6.9	(15)	3.61	(10)	2.18	(10)	421	...	5.5	5.1	4.70	90	5.77	6.66	2.89	110
113	$(NH_4)_3Fe(C_2O_4)_3$	7.0	(50)	3.62	(12.5)	3.19	(12.5)	420	...	5.6	4.59	4.20	83	6.3	4.10	3.67	76
114	$Fe(NH_4)(SO_4)_2<12H_2O$	7.0	(15)	9.2	(10)	8.2	(7)	439	...	6.8	3.53	4.75	72	7.4	3.33	2.55	69
115	$Na_4Fe(CN)_6.10H_2O$	7.4	(12.5)	2.04	(10)	3.51	(9)	810	...	7.1	4.37	3.73	81	7.6	6.2	8.4	105
116	$Fe(C_3H_5O_3)_2.3H_2O$	9.5	(40)	5.2	(15)	4.50	(6)	415	...	8.4	6.2	7.6	105	7.7	10.0	5.1	118
117	Ferric Salicylate	9.8	(20)	3.51	(15)	5.1	(12.5)	431	...	8.7	2.73	3.12	51	8.2	7.0	9.2	114
118	$Fe[(CH_3)_2AsO_2]_3$	10.0	(15)	5.1	(10)	7.7	(8)	406	...	9.2	7.0	8.2	114	10.4	2.65	1.54	43

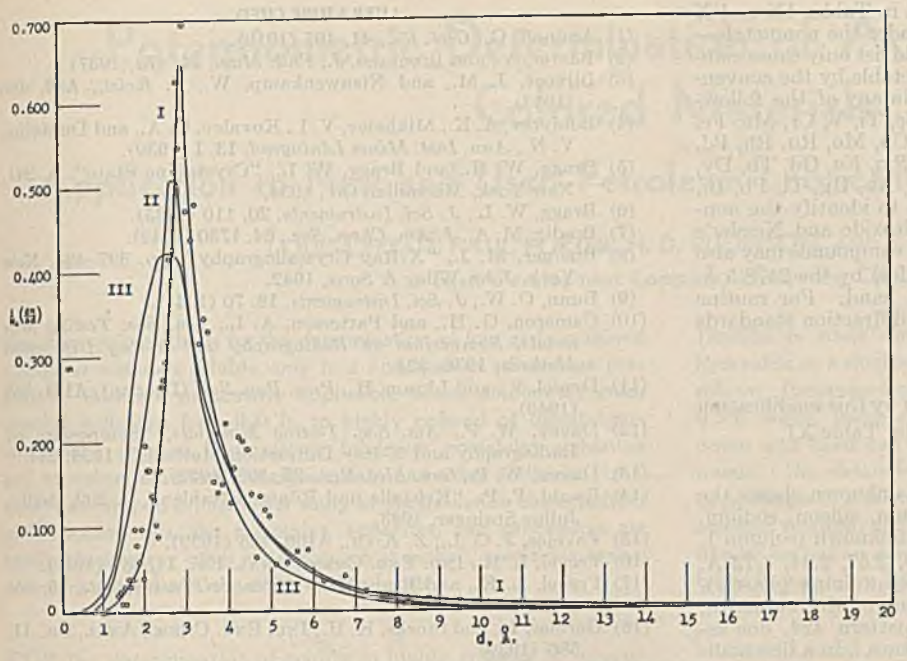

Figure 3. Distribution of Interplanar Spacings of Reference Lines

I refers to distribution of first reference line of various standards with respect to d, interplanar spacing; II and III pertain to second and third reference lines, respectively. N_0 = total number of cataloged standards = 2100. $(dN)_{I,d}$ = number of standards having their first reference line located in interval $\left(d \pm \frac{\Delta d}{2}\right)$. For sake of clarity experimental points are shown only for I. Maxima for I, II, and III occur at 2.95 ± .08, 2.75 ± .20, and 2.60 ± .30 Å., respectively. n = number of diffraction lines per pattern; $4 \leqslant n \leqslant 45$; $\bar{n} = 19$. I_r = intensity of rth reference line; $2 \leqslant \bar{I}_1 \leqslant 212$ based on I_1 (NaCl) = 150. $\bar{I}_1:\bar{I}_2:\bar{I}_3$ = 42.3:25.7:20.2 for MoKα (when corrected for factor $\frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}$, continued ratio is proportional to 26.0:-22.0:19.2). ν_1 expresses probability that $d_1 > d_2$ or d_3; $\bar{\nu}_1:\bar{\nu}_2:\bar{\nu}_3$ = 1.00:50:0.28. A bar above a letter signifies an arithmetic average for N_0 standards.

that for most common inorganic substances the reference lines fall within the interval 2.0 to 3.5 Å. Considering the first reference line, one finds 15 patterns listed in the interval 15 to 20 Å. and 74 patterns in the interval 2.95 to 3.00 Å. (of course, the second and third reference lines of a substance materially reduce the number of standards to be considered). In the identification of mixtures, however, a crowding of reference in the relatively narrow interval from 2.6 to 3.0 Å. might necessitate an undue amount of searching to locate the sought standard patterns in a very large collection of standards. The point may be visualized by the diffraction pattern of a binary mixture for which there are six reference lines, the intensities of which may be denoted by I_r and ζ_s where $r, s = 1, 2, 3$. Assuming (1) that there are no superpositions of lines, (2) that the six most intense reflections are also the six reference lines for the binary mixture, and (3) that $I_1 \geqslant I_2 \geqslant I_3 \geqslant \zeta_1 \geqslant \zeta_2 \geqslant \zeta_3$; $\cap$, one may have to exhaust from 1 to 119 possible combinations to find the appropriate set of reference lines for one component [for an n-component mixture there are $3n(3n - 1)(3n - 2) - (n - 1)$ combinations]. In the general case of a binary mixture, allowance must also be made for the following possibilities: (1) the superposition of reference lines, for example, the second reference line of phase A and the third reference line of phase B so that $I_2 + \zeta_3 > I_r$ or ζ_s; (2) the superposition of a reference line of phase A and a moderately intense reflection of phase B $(I_3 + \zeta_4 > I_2)$; and (3) the presence of prominent nonreference lines for phase A, so that I_4 or $I_{4+n} > \zeta_2$. These considerations are general and apply to any scheme of classification.

In case the number of standards exceeds 10,000 to 20,000, the problem may arise as to how to circumvent the probable congestion of reference lines and the multiplicity of trial reference lines for multicomponent mixtures. In view of the fact that the great majority of analyses are supplemented or confirmed by qualitative spectroscopic analysis, it may be expedient to reverse the procedure and obtain the spectroscopic data first to facilitate finding the appropriate diffraction standards.

For example, all compounds containing aluminum would be grouped under aluminum as shown in Table IX. Those substances containing both aluminum and iron would be listed under

Table XI. Powder Diffraction Data

Filtered MoKα used to obtain diffraction patterns. d = interplanar spacing. I = peak intensity of a diffraction line. I/I_1 = relative intensity, where I_1 is intensity of strongest line of particular phase in question (values in parentheses refer to calculated intensities). Diffraction pattern of albite, Amelia Court House, Va., was taken with a 0.1-mm. slit to resolve some of the broader reflections.

Spectroscopic Analysis of Unknown. Fe, Al, Si, Na chief constituents; minor constituents P 0.1 to 0.5%, K 0.01 to 0.1%, Ca 0.001 to 0.01%.

Unknown		Albite, $NaAlSi_3O_8$		Phase I	Goethite, α-FeO.OH		Phase II		$NaAlSi_3O_8$, Albite, Amelia Court House, Va.	
d, Å.	I	d, Å.	I/I_1	I/I_1	d, Å.	I/I_1	I/I_1	ΣI	d, Å.	I/I_1
6.5	1	6.4	0.08	0.02	..	..	..	..	6.4	0.06
5.0	3	..	..	..	4.98	0.04	0.09	..	5.9	0.04
4.20	25	..	..	..	4.21	1.00 (25)	0.76	..	5.5	0.02
4.02	12.5	4.05	0.35	0.28	..	..	..	..	4.01	0.50 (50)
3.80	3	3.80	0.16	0.07	..	..	..	..	3.84	0.06
3.67	9B	3.66	0.25	0.20	..	..	..	..	3.76	0.08
3.38	4	..	..	..	3.39	0.12	0.12	..	3.66	0.40 (40)
3.19	50	3.20	1.00 (50)	1.14	..	..	..	..	3.50	0.10
2.95	12.5	2.96	0.25	0.28	..	..	..	..	3.37	0.08
2.69	12.5	2.65	0.02	(1)	2.70	0.36	0.38	..	3.19	1.00B (100)
2.57	12.5	2.56	0.12	(5)	2.58	0.24	(8)	13	2.94	0.20B
2.44	30	2.44	0.14	(6)	2.45	0.80	(26)	32	2.85	0.10
2.37	1	..	..	..	..	..	..	..	2.64	0.04
2.32	2	2.32	0.12	0.05	..	..	..	..	2.55	0.10
2.25	5	..	..	..	2.25	0.12	0.15	..	2.43	0.10
2.18	6	2.18	0.06	(3)	2.19	0.20	(7)	10	2.38	0.04
2.10	3B	2.13	0.12	0.07	..	..	..	..	2.31	0.10B
2.01	4	1.99	0.08	0.09	..	..	..	..	2.24	0.01
1.90	5B	1.90	0.12	(5)	1.92	0.08	(3)	8	2.19	0.02
1.81	6B	1.83	0.18	(8)	1.80	0.08	(3)	11	2.12	0.08
1.72	17.5	1.73	0.08	(4)	1.72	0.36	(12)	16	2.06	0.06
1.60	4	..	..	..	1.60	0.08	0.12	..	1.98	0.06B
1.56	15	1.58	0.12	(5)	1.56	0.28	(9)	14	1.89	0.10
1.51	12.5	1.50	0.08	(4)	1.50	0.24	(8)	12	1.85	0.08
1.455	10	1.460	0.16	(7)	1.455	0.12	(4)	11	1.82	0.10
1.419	9	1.425	0.16	(7)	1.420	0.04	(1)	8	1.782	0.08
1.350	4	1.350	0.14	(6)	1.355	0.08	(3)	9	1.743	0.04
				$(I_1)_I \approx (44)$			$(I_1)_{II} \approx (33)$		1.720	0.04

aluminum and iron—e.g., $FeAl_2O_4$ is listed in Tables IX and X (there are nine such substances listed). Under the nonmetals—H, C, N, O, F, S, Cl, Se, Br, Te, I—one would list only those compounds which do not contain elements detectable by the conventional arc spectra—i.e., which do not contain any of the following: Li, Be, B, Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Cb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Ra, Th, U. Chemical tests are convenient to identify the nonmetals—e.g., the use of aqueous sodium hydroxide and Nessler's reagent to detect ammonium salts. Organic compounds may also be detected in the arc (using copper-electrodes) by the 2478.5 Å. emission line of carbon and the cyanogen band. For routine analysis it would be advisable to check the diffraction standards listed under carbon and nitrogen.

The procedure for identifying an unknown by this modification of the triple index system (*25*) is illustrated by Table XI.

Qualitative spectroscopic analysis of the unknown shows the following chief constituents: iron, aluminum, silicon, sodium. The more prominent diffraction lines of the unknown (column 1, Table XI) are: 4.20, 4.02, 3.19, 2.95, 2.69, 2.57, 2.44, 1.72 Å. Looking under Table X to locate the iron-containing phase(s), one finds α-FeO(OH) as a likely component of the unknown. Checking the complete data of standard pattern 424, one establishes the presence of goethite in the mixture. In a like manner Table IX indicates albite, $NaAlSi_3O_8$, as the second phase of the unknown. The presence of albite also could have been ascertained by looking under the index for sodium or silicon. As all the diffraction lines of the unknown are satisfactorily accounted for, the qualitative compound analysis is considered complete and there is no need to check the diffraction standards listed under carbon, nitrogen, etc.

The extent to which the suggested classification of diffraction standards by elements circumvents the anticipated congestion of reference lines can be estimated by an examination of Tables IX and X in regard to the number of times the average compound is listed under more than one element.

For aluminum (Table IX) there are 18 substances listed only once (under aluminum), 47 substances listed twice (distributed over 23 elements), 11 substances listed three times (distributed over 8 elements), and two substances listed 4 times (distributed over 5 elements). For Table X there are 39 substances indexed only under iron, 60 substances indexed twice (distributed over 23 elements), 13 substances listed three times (distributed over 19 elements), and five minerals listed 4 times (distributed over 11 elements). A calculation of the quotient

$$\frac{\sum_r r n_r}{N \sum_r n_r}$$

where n_r = number of substances listed r times
N = total number of elements under which the various substances are indexed

shows that the congestion of references lines has been reduced by a factor of 12.7 for the aluminum compounds and 13.9 for the iron compounds.

However, it appears that the intrinsic advantage of combining spectroscopic information with diffraction data is the natural incorporation of isomorphous groups in the various tables. This combination of empirical standards and structural types into one index should broaden the scope and utility of chemical analysis by powder diffraction.

ACKNOWLEDGMENT

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Potentiometric Determination of Acidity in Highly Colored Materials

Application to New and Used Petroleum Lubricants Containing Additives

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Potentiometric methods for the determination of free and combined acidity of materials soluble only in a nonaqueous solvent are presented; they are particularly applicable where acidimetric color titration indicators fail—that is, to highly colored or opaque materials such as used lubricants or lubricants containing oxidation and corrosion inhibitors, detergents, fats, and other additives. Although developed primarily for study of the oxidation characteristics of lubricating oils, the principles, apparatus, and procedures are applicable to many other materials such as asphalt, emulsions, resins, polymers, animal and vegetable fats, oils, etc.

Titration is made directly or after saponification with potassium hydroxide in a single-phase solution of the sample in a nonaqueous solvent (benzene–isopropyl alcohol) containing approximately 0.5% water, using a glass–calomel electrode system. Inflection points and fixed cell potentials are used for the estimation of end points. The determination by a single titration of two or more components of a mixture of acids or bases not distinguishable in an aqueous titration, and phenomena which make possible the estimation of ionization constants of acids and bases having limited solubility in water, are briefly described.

FOR the determination of acidity in highly colored or opaque materials methods that depend upon indicator color change are inadequate and often useless, even though they may be applicable to colorless materials insoluble in water or ethyl alcohol. The potentiometric method for the determination of neutralization end points, the logical alternative, seems especially promising when considered in conjunction with a titration solvent that is capable of dissolving or dispersing a suitable portion of water-insoluble material. While the present discussion deals with petroleum products such as heavy oils, asphalts, resins, and the like, the principles are equally applicable to many other commercial materials.

A potentiometric method which is both sound in principle and readily applicable in practice should combine several important characteristics. The electrodes should be sturdy and readily give reproducible values in identical solutions, but should not be attacked by dilute acid or base solutions or organic materials, be subject to atmospheric oxidation, or appreciably contaminate the titration solvent. The potential difference of the electrode system should be nearly proportional to the hydrogen-ion activity of the mixture of titration solvent and sample, and equilibrium should be attained in a conveniently short time. The titration solvent should completely dissolve an adequate amount of sample and this mixture should tolerate the presence of several milliliters of water from the sample without formation of a second phase. The titration medium should have a low inherent acid value, and should be inert to prolonged action of strong bases, strong acids, salts, metals, glass, and atmospheric materials. The polar properties of the solvent should be such that dissolved acidic materials, with dissociation constants greater than 10^{-7} when dissolved in water, will ionize sufficiently to permit neutralization by the addition of an equivalent quantity of an alcoholic strong base solution. The titration solvent should be sufficiently conductive to allow only momentary accumulation of electrostatic charges when a low-resistance reference electrode is immersed in it.

While there have been many noteworthy contributions on the potentiometric titration of acids in nonaqueous solutions (*1–37*), no published method entirely fulfills the above conditions.

The hydrogen electrode is slow, troublesome, and easily poisoned by a variety of materials (*8, 32*). Although the quinhydrone electrode has found repeated application in nonaqueous solutions (*5, 6, 11, 13, 19, 30, 31, 35*), it cannot be used in all solvents; it is attacked by dissolved oxygen, and is not reliable in alkaline solutions. The antimony electrode functions well as an indicating electrode (*20*), but is not reproducible from time to time and is not universally applicable; this is generally true of all similar metal electrodes (*33*). Platinum-tungsten (*28*), platinum-carbon (*27*), and other dissimilar electrode pairs (*4, 9*) function only in systems that show distinct, sudden changes in hydrogen-ion activity; they are easily influenced by extraneous materials. The thin unshielded glass electrode (*7, 12, 14, 29*) is reproducible and accurate, but undesirably fragile. The modern high-resistance glass electrode has ample mechanical strength, but requires adequate shielding in order to avoid error due to electrostatic influences, and is not applicable in completely anhydrous solvents (*12*).

The saturated calomel electrode, in various forms, is generally desirable as a reference electrode when used with a suitable salt bridge. The agar-agar salt bridge is appreciably attacked by organic solvents and must be renewed at frequent intervals (*6, 11, 29, 30*). The aqueous salt bridge with a ground-glass joint contact is generally reproducible, if properly prepared and maintained. The use of a nonaqueous salt bridge is feasible (*3, 12, 16, 20, 30*) and desirable, but further work is needed to establish satisfactorily the application of the nonaqueous reference electrode. In some instances, the silver–silver chloride electrode (*11, 12, 13, 31*) is a satisfactory reference but it is very slow in attaining equilibrium and gives a distorted potential–volume titration curve.

The potentiometric methods given in this paper have proved satisfactory for determining the free and combined acidic, or basic, constituents present in new or oxidized petroleum oils and in other petroleum products. The free acidity, or basicity, is determined by potentiometrically titrating the sample dissolved in a benzene–isopropyl alcohol solution, using a glass–calomel electrode system. The combined acidity is similarly determined by potentiometric titration with alcoholic acid after saponifying the sample dissolved in a benzene–isopropyl alcohol solution containing an excess of strong base. These methods are applicable to materials that are soluble, or nearly soluble, in benzene–isopropyl alcohol mixtures, and that are colorless, colored, or produce colored solutions during the determination. Unchanged compounds that are only weakly acidic or basic, and whose dissociation constants, K_a or K_b, in water are equal to or less than $K = 10^{-9}$, are not detectable and do not interfere. Various acid or base groups may be distinguished, provided there is a satisfactory difference between the dissociation constants of the groups. Thus strong acids, such as hydrochloric, are distinguishable from weak acids, such as formic and acetic, which in turn are distinguishable from weaker acidic materials such as thiophenol. Similar relationships hold for basic groups of like differences in basicity. Covering a period of four years, these methods have been successfully used for the determination of free and combined acidity in new and oxidized motor oils, turbine oils, oil additives, motor oil sludges, asphaltenes, crude oils, asphalt, asphalt resi-

dues, distillates, distillate bottoms, polymers, rubber, soaps, vegetable and animal oils, fats, waxes, greases, common solvents, and water solutions.

The applicability of the glass electrode to the measurement of hydrogen-ion activity in nonaqueous solutions has been frequently questioned from a theoretical viewpoint. However, titration curves made in nonaqueous solution using the glass–calomel electrode pair are perfectly reproducible, and are usable for accurately measuring the acid or base content of the solutions. To avoid confusion of titration data obtained in nonaqueous media with those obtained in water, a new unit, the cG unit, has been coined to replace the pH unit in nonaqueous media.

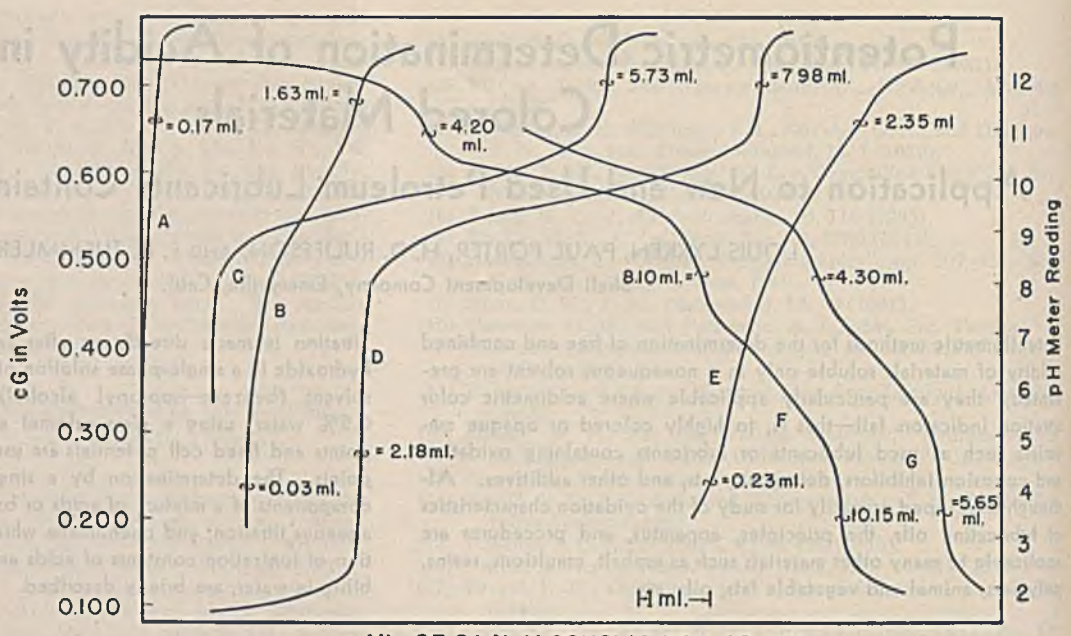

Figure 1. Illustrative Titration Curves for Determination of Free Acids and Bases

Potentiometric titration with base
A. Blank
B. 10 grams of oxidized oil
C. Naphthenic acids
D. Hydrochloric and naphthenic acids
E. 5 grams of asphalt

Potentiometric titration with acid
F. 5 grams of alkaline oil containing free caustic
G. 5 grams of alkaline oil

Titration cell. Glass electrode || saturated calomel electrode
Titration solvent. 50 ml. of benzene and 50 ml. of isopropyl alcohol containing 1% water

It has been found (*10, 17*) that the potential of a glass electrode in aqueous media depends upon the hydrogen-ion activity of the solution according to the equation (at 25° C.):

$$E_G = E_G^\circ + 0.0591 \log (H^+ \text{ activity})$$

Assuming that the potential of the glass electrode varies in a similar manner with the hydrogen-ion activity in nonaqueous solution, the following equation can be considered valid:

$$E_G = E_G^\circ + cG$$

The value of E_G° for any particular glass electrode is constant. Under suitable conditions and assuming that liquid junction effects are negligible, the potential of a saturated calomel electrode is constant, and not dependent upon the hydrogen-ion activity or upon the activity of any other dissolved substance. Therefore

$$E = E_C^\circ + E_G^\circ + cG$$

$$E = E_{GC} + cG$$

where E is the measured electromotive force between the electrodes and E_{GC} is a constant which must be determined by calibration for each electrode pair.

Methods for Free and Combined Acid and Base Numbers

Since complete details of these methods are available (*1, 2*), only a brief outline is included here.

APPARATUS

The following apparatus has been found through experience to be most satisfactory:

Meter. The electronic voltmeter (*26*), the dual alternating current titrometer described by Penther and Rolfson (*25*), or the Beckman model M or Model O industrial pH meters.

Electrodes. High-resistance glass electrode No. 4990, and the sleeve-type calomel electrode, No. 4970A, manufactured by the National Technical Laboratories, and supplied on Beckman meters.

Titration Stand, described by Lykken and Rolfson (*21*).

Refluxing Apparatus. Regular saponification apparatus including hot plate, Allihn-type condenser, and 300-ml. Erlenmeyer flask, or the special apparatus pictured in Figure 3 of (*2*).

REAGENTS

Standard 0.1 N and 0.2 N potassium hydroxide in isopropyl alcohol. Standard 0.1 N and 0.2 N hydrochloric acid in isopropyl alcohol. Standard aqueous pH = 4 buffer. Standard nonaqueous cG = 0.650-volt buffer (*2*). Standard nonaqueous cG = 0.236-volt buffer (*2*).

Titration Solvent. Mixture of equal volumes of c.p. benzene and c.p. isopropyl alcohol containing 1% water.

CHARACTERISTICS OF ELECTRODE SYSTEM

The glass-calomel system requires constant and regular attention to obtain reproducible values. After every titration the electrodes must be rinsed thoroughly with benzene–isopropyl alcohol and water, carefully dried with a clean towel, and soaked for a short time in distilled water. Special care must be taken in preparing the ground-glass sleeve of the calomel electrode.

Before use, the electrode pair is standardized with aqueous pH = 4 buffer, and calibrated with two nonaqueous buffers (*2*), cG = 0.650 and 0.236 volt. The constant E_{GC} is calculated from the expression:

$$E_{GC} = E - 0.236$$

where E is the voltage of the cell when immersed in pH = 4 buffer.

PROCEDURE FOR FREE ACID (ACID NO.)

Weigh or pipet a sample of less than 20 grams containing from 0.2 to 0.5 milliequivalent of acid into a tall-form 250-ml. electrolytic beaker, add 100 ml. of titration solvent, and adjust the beaker so that the electrodes are immersed in the solvent. Titrate with 0.1 N alcoholic potassium hydroxide, making certain that sufficient time is allowed for equilibration between increments of caustic. A satisfactory indication of equilibrium is a cell voltage "drift" of less than 5 millivolts per minute. Plot a graph of milliliters of potassium hydroxide as abscissas, and millivolts or pH scale readings as ordinates. Mark inflections that occur in the neighborhood of cG = 0.236 and 0.650 volt (corresponding to pH scale readings of 4.0 and 11.0, respectively). Determine the number of milliliters required to each break. Make a blank titration following the above directions, but omitting the sample.

When the titration curve of the sample shows no definite inflection point, the number of milliliters of potassium hydroxide used to obtain cG readings of 0.236 and 0.650 volt are taken as equivalent to the amounts of strong and total acids, respectively. The voltages between the electrodes corresponding to cG = 0.650 and 0.236 volt, as calculated using the constant E_{GC} may

be used as the correct values for any series of determinations with a given electrode system. For work of a special nature or for cooperative or referee testing, the voltages corresponding to these cG values should be obtained by calibration with standard nonaqueous buffers.

PROCEDURE FOR FREE BASE (BASE NO.)

Proceed exactly as for free acid, using 0.1 N hydrochloric acid instead of potassium hydroxide.

CALCULATIONS FOR FREE ACID AND FREE BASE

Figure 1 gives acid and base titration curves which illustrate the typical shapes commonly encountered and the manner of locating end points. The amount of base needed to neutralize the acids up to the first end point near $cG = 0.236$ volt less the equivalent blank titration is a measure of the acid constituents with strong acid characteristics. The amount of base needed to neutralize the acids between the end points near $cG = 0.236$ and 0.650 volt less the equivalent blank titration is a measure of the acid constituents with weak acid characteristics. Basic materials neutralized by hydrochloric acid above the end point near $cG = 0.650$ are strong bases and those neutralized between the end points near $cG = 0.650$ and 0.236 volt are weak bases.

PROCEDURE FOR COMBINED ACIDS AND BASES (SAPONIFICATION NO.)

General Procedure. Although this procedure is the most general one, it is used only for samples of unknown saponification characteristics or for samples that upon saponification produce an adherent precipitate which clings to the surface of the reflux vessel. The simplified direct titration procedure is generally preferred whenever it is applicable because it allows a considerable saving of time and manipulative effort.

Weigh or pipet a sample containing from 1 to 3 milliequivalents of combined acid or base into a suitable reflux vessel. Add boiling chips, 40 ml. of c.p. benzene, and 40 ml. of 0.2 N alcoholic potassium hydroxide. Reflux gently for 2 hours, remove from the hot plate, cool, and transfer the contents to a titration beaker. Adjust the beaker so that the electrodes are immersed in the solvent, and titrate with 0.2 N alcoholic hydrochloric acid as directed in free base determination. Select the strong base and weak base end points in the same way as for free base (above). To recover caustic or weak bases left adhering to the walls of the reflux vessel, add 100 ml. of water, cover the vessel, and bring to a boil. Cool the water solution, pour into a titration beaker, place the beaker upon the titration stand, and titrate with 0.2 N alcoholic hydrochloric acid. On the water titration curve select the end points near the cG potentials of 0.49 and 0.30 volt (pH 8.2 and 5.0, respectively). Add the number of milliliters of hydrochloric acid required for the upper break in the aqueous titration curve to the number of milliliters required for the upper break in the nonaqueous titration curve, and the number of milliliters for the lower break in the aqueous titration curve to the corresponding number in the nonaqueous titration curve.

Make a blank determination using the above procedure, but omitting the sample.

Direct Titration Procedure. Carry out the determination as directed in the general procedure, but add sample, caustic, and benzene directly to the titration beaker, reflux in an apparatus with an immersion-type condenser, cool, and titrate directly in the reflux beaker.

CALCULATIONS FOR COMBINED ACIDS AND BASES

Figure 2 gives typical combined acid-base titration curves which illustrate the shapes commonly encountered and the method of selecting end points. Where no definite breaks are obtained, the arbitrary points at which $cG = 0.650$ and 0.236 volt are selected as in the free acid procedure.

The difference in the amount of standard acid required to produce the end point near cG potential 0.650 volt (pH scale reading of 11.0) for the sample and the blank determinations is a measure of the amount of free and combined acidic constituents in the sample; this difference is equivalent to the customary saponification number. The difference in the amount of standard acid required to produce the end point near cG potential of 0.24 volt (pH scale reading of 4.0) for the sample and blank determinations is a measure of the free and combined strong acid constituents in the sample if the blank titration is greater than the sample titration; if the sample titration is greater than the blank titration, the difference between them is a measure of the basic constituents present in the sample. These relationships do not apply if the sample contains strong acids or bases, along with constituents that upon saponification produce bases or acids, respectively.

In those cases in which a water solution is prepared and titrated, the amount of standard acid used to produce an end point near cG potential of 0.485 volt (corresponding to pH 8.2) in the water solution titration is added to that required to produce an end point near a cG potential of 0.650 volt (corresponding to pH scale reading of 11.0) in the benzene–isopropyl alcohol solution

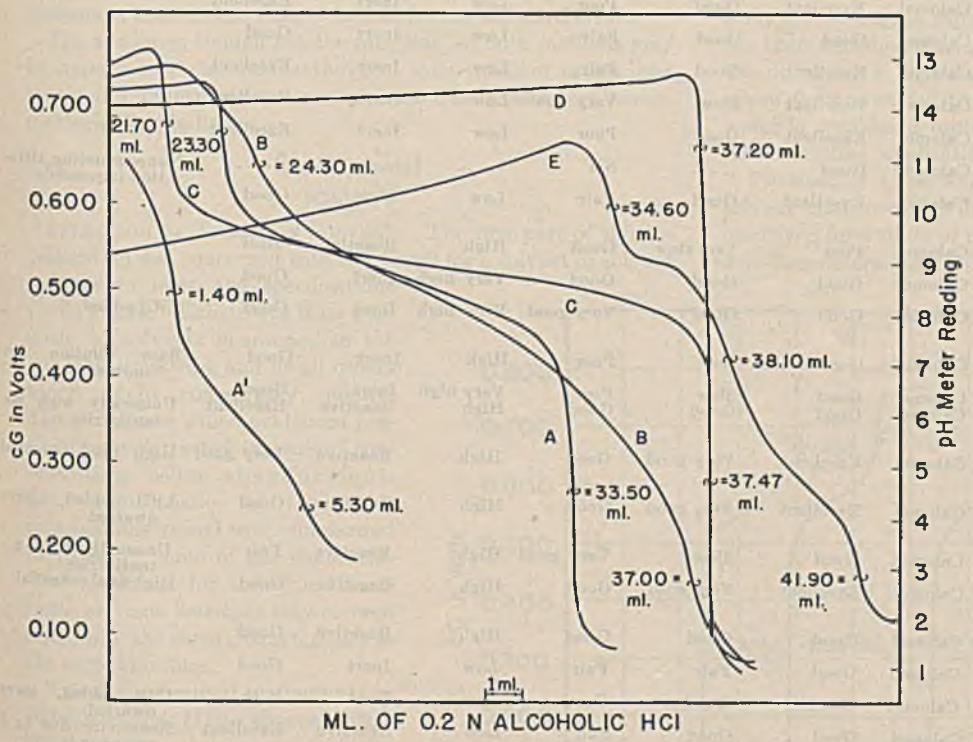

Figure 2. Illustrative Titration Curves for Determination of Combined Acids and Bases

Potentiometric titration with alcoholic hydrochloric acid of basic constituents remaining after saponification with potassium hydroxide

A. Rapeseed oil, titration of nonaqueous saponification mixture
A'. Rapeseed oil, titration of water-soluble residue remaining in saponification vessel
B. Oxidized oil, titration of nonaqueous saponification mixture directly in reflux vessel
C. Castor oil, titration of nonaqueous saponification mixture directly in reflux vessel
D. Blank, titration of nonaqueous saponification mixture directly in reflux vessel
E. Alkaline oil, titration of nonaqueous saponification mixture directly in reflux vessel

Titration cell. Glass electrode || calomel electrode
Saponification medium. 50 ml. of benzene, 50 ml. of isopropyl alcohol

titration. Similarly, the amount of standard acid used to produce an end point near *cG* potential of 0.295 volt (corresponding to pH 5.0) in the aqueous titration is added to that required to produce an end point near a *cG* potential of 0.236 volt (corresponding to pH scale reading of 4.0) in the nonaqueous titration. These sums are used to calculate the various differences and the calculations are then made as though only one titration curve had been obtained.

ACCURACY AND PRECISION

The accuracy and precision of the free acidity method depend upon the acids present, and upon the materials associated with the acids. In the determination of naphthenic acids in 10 grams of lubricating oil, the standard deviation is less than 0.05 ml. of 0.1 *N* alkali, and the systematic error is less than ±1.96 times the standard error.

The accuracy and precision of the combined acidity method

Table I. Electrochemical Characteristics of Various Nonaqueous Solvents

Solvent Composition	Water Added, Ml.	Electrodes: Indicating	Electrodes: Reference	Solvent Action for Heavy Oil	Equilibrium Rate of Electrodes	Electrical Conductivity	Inherent Acidity of Solvent	Chemical Stability of Solvent	Nature of Inflection Point	Remarks
100 ml. $(CH_3)_2CHOH$	10	Glass	Calomel	Poor	Very good	Good	Low	Inert	Excellent	Standard of reference
100 ml. $(CH_3)_2CHOH$	1	Glass	Calomel	Fair-poor	Very good	Fair	Low	Inert	Excellent	
100 ml. $(CH_3)_2CHOH$	None	Glass	Calomel	Fair-poor	Good	Fair	Low	Inert	Excellent	Equilibrium slow in break
15 ml. $CHCl_3$ + 90 ml. $(CH_3)_2CHOH$	1.5	Sb	Calomel	Good	Good	Good	Low	Slightly reactive	Good	
25 ml. $CHCl_3$ + 75 ml. $(CH_3)_2CHOH$	0.75	Glass	Calomel	Very good	Good	Good	Low	Slightly reactive	Excellent	Little acid formed during titration
50 ml. $CHCl_3$ + 100 ml. $(CH_3)_2CHOH$	1	Glass	Calomel	Good	Good	Good	Low	Reactive	Good	Little acid formed during titration
50 ml. $CHCl_3$ + 100 ml. $(CH_3)_2CHOH$	1	Sb	Calomel	Good	Good	Very good	Low	Reactive	Good	LiCl added
75 ml. $CHCl_3$	None	Sb	Calomel	Very good	Slow	Very poor	Low	Reactive	Good	Acid formed during titration
75 ml. $CHCl_3$	0.015	Sb	Calomel	Excellent	Slow	Good	Low	Very reactive	Poor	LiCl added, much base consumed
75 ml. $CHCl_3$ + 25 ml. $(CH_3)_2CHOH$	None	Sb	Calomel	Very good	Slow	Fair	Low	Reactive	Very poor	Acid formed during titration
75 ml. $CHCl_3$ + 35 ml. $(CH_3)_2CHOH$	0.1	Glass	Calomel	Very good	Slow	Good	Low	Reactive	Very poor	Acid formed during titration
100 ml. $CHCl_3$ + 10 ml. $(CH_3)_2CHOH$	1	Glass	Calomel	Very good	Slow	Poor	Low	Reactive	Very poor	Acid formed during titration
75 ml. CCl_4	None	Sb	Calomel	Excellent	Slow	Very poor	Low	Very reactive	Good	Acid formed during titration
75 ml. CCl_4 + 35 ml. $(CH_3)_2CHOH$	1	Glass	Calomel	Very good	Slow	Poor	Low	Reactive	Fair	
75 ml. CCl_4 + 35 ml. $(CH_3)_2CHOH$	1	Sb	Calomel	Very good	Slow	Poor	Low	Very reactive	Poor	Acid formed during titration
100 ml. C_6H_6	None	Glass	Calomel	Excellent	.....	Nil	.....	.....	.....	Nonconducting, titration impossible
50 ml. $(CH_3)_2CHOH$ + 50 ml. C_6H_6	None	Glass	Calomel	Excellent	Good	Poor	Low	Inert	Excellent	
50 ml. C_6H_6 + 50 ml. C_2H_5OH	0.5	Glass	Calomel	Good	Good	Fair	Low	Inert	Good	
75 ml. C_6H_6 + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Excellent	Good	Fair	Low	Inert	Excellent	
75 ml. C_6H_6 + 25 ml. $(CH_3)_2CHOH$	None	Glass	Calomel	Excellent	Slow	Very poor	Low	Inert	Excellent	
75 ml. C_6H_6 + 25 ml. $(CH_3)_2CHOH$	0.3	Glass	Calomel	Excellent	Good	Poor	Low	Inert	Excellent	
100 ml. petroleum ether	None	Glass	Calomel	Good	.....	Nil	.....	.....	.....	Nonconducting, titration impossible
75 ml. petroleum ether + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Excellent	Good	Fair	Low	Inert	Good	
75 ml. *n*-butyl alcohol 75 ml. acetone	None	Glass	Calomel	Poor	Very slow	Good	High	Reactive	Good	
75 ml. *n*-butyl alcohol 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Good	Good	Good	Very high	Inert	Good	
75 ml. *n*-butyl alcohol + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Good	Good	Very good	Very high	Inert	Good	LiCl added
75 ml. cyclohexanol + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Good	Slow	Poor	High	Inert	Good	Base dilution not "normal"
150 ml. cyclohexanol	1	Glass	Calomel	Good	Slow	Poor	Very high	Inert	Good	
50 ml. methyl ethyl ketone + 25 ml. $(CH_3)_2CHOH$	0.025	Glass	Calomel	Good	Good	Good	High	Reactive	Excellent	Unusually high potential rise
75 ml. methyl ethyl ketone + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Excellent	Very good	Good	High	Reactive	Very good	High final potential
75 ml. methyl ethyl ketone + 75 ml. $(CH_3)_2CHOH$	0.8	Sb	Calomel	Excellent	Very good	Good	High	Reactive	Good	LiCl added, curve dwarfed
100 ml. methyl ethyl ketone	None	Glass	Calomel	Good	Slow	Very good	High	Reactive	Fair	Unusually high potential rise
100 ml. methyl ethyl ketone + 50 ml. $(CH_3)_2CHOH$	5	Glass	Calomel	Excellent	Very good	Good	High	Reactive	Good	High final potential
75 ml. amyl ketone + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Good	Good	Good	High	Reactive	Good	
50 ml. anisole + 100 ml. $(CH_3)_2CHOH$	1	Glass	Calomel	Good	Fair	Fair	Low	Inert	Good	
50 ml. anisole + 100 ml. $(CH_3)_2CHOH$	1	Sb	Calomel	Good	Good	Good	Low	Inert	Poor	LiCl added, curve dwarfed
75 ml. isopropyl ether + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Good	Good	Fair	Low	Reactive	Excellent	Reactivity due to S compounds
75 ml. isopropyl ether + 75 ml. $(CH_3)_2CHOH$	0.8	Sb	Calomel	Good	Good	Good	Low	Reactive	Excellent	LiCl added
75 ml. dioxane + 75 ml. $(CH_3)_2CHOH$	0.8	Glass	Calomel	Good	Slow	Fair	.....	.....	None	
95 ml. dioxane	5	Glass	Calomel	Good	Slow	Good	.....	.....	Very poor	Good inflection for strong acid break
100 ml. benzyl alcohol	None	Glass	Calomel	Excellent	Very slow	Fair	Very high	Reactive	Very good	Medium has high viscosity

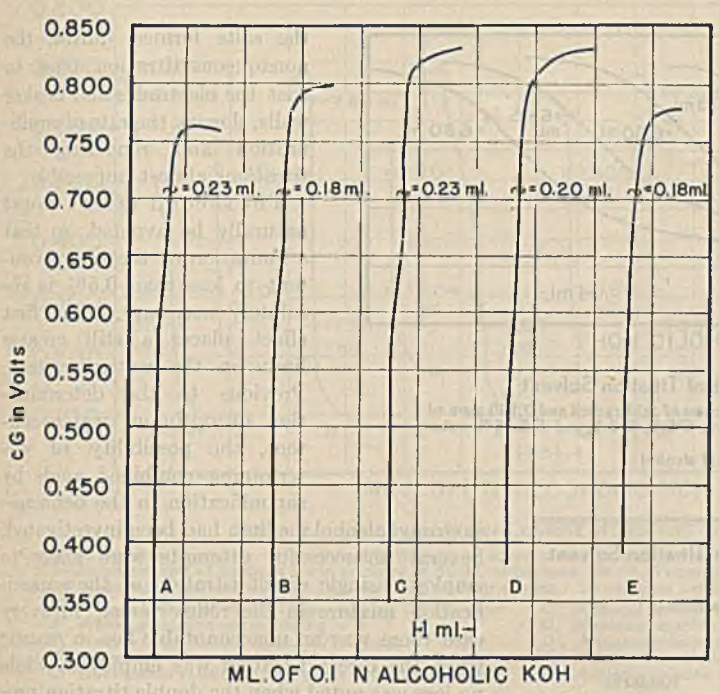

Figure 3. Optimum Water Content of Titration Solvent

Free acid-base procedure. Potentiometric titrations of inherent acidity of solvent containing: *A* 0.05, *B* 0.5, *C* 2.5, *D* 5.0, and *E* 9.6% water
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol

depend upon the esters and acids present, and upon the materials associated with the esters. In the determination of the saponification number of castor oil in 10 grams of lubricating oil, the standard deviation is less than 0.05 ml. of 1.0 *N* acid, and the systematic error is less than ±1.96 times the standard error.

The accuracy, though not the precision, of both methods may be impaired by the nonreactivity of some acids or esters, and by the insolubility of some materials such as certain high molecular weight asphaltenes.

Experimental

SOLVENT

Selection of Titration Solvent. The first part of this investigation was concerned with the search for a solvent or solvent mixture to meet the specifications stated above. Exhaustive tests were made of solvents mentioned in the available literature, and of all others which might conceivably qualify. Those mixtures which evidenced possibilities were tested in various concentrations before abandonment. The characteristics of the major compositions tested are summarized in Table I; some of the concentration variations for individual mixtures are not listed, as they showed essentially the same characteristics as the parent mixture.

The study resulted in finding two suitable media: (1) an approximately 50% mixture of benzene and isopropyl alcohol, and (2) an approximately 50% mixture of petroleum ether and isopropyl alcohol. The benzene–isopropyl alcohol was chosen because it has greater water tolerance and is a better solvent for asphalts and oxidized materials.

Optimum Water Concentration of Titration Solvent. The presence of a certain amount of water in the benzene–isopropyl alcohol medium is beneficial, since it greatly reduces the resistance of the mixture and makes the measurement of potential difference between the electrodes considerably easier. A study was made of the optimum water content of the solvent for use in the free and combined acid methods already described.

Titration of Free Acid or Base. Mixtures of benzene and isopropyl alcohol were prepared containing 0.05, 0.5, 2.5, 5.0, and 9.6 (saturated) % water, and used as titration solvents in the following titrations:

Blank titrations. One hundred milliliters of each solvent were titrated with 0.0852 *N* alcoholic potassium hydroxide.

Hydrochloric acid–naphthone A titrations. Samples of 2 ml. of 0.1 *N* alcoholic hydrochloric acid and 2 ml. of 0.065 *N* alcoholic naphthone A (naphthenic acid) were dissolved in 100 ml. of each solvent-water mixture and titrated with 0.0852 *N* alcoholic potassium hydroxide.

Zinc soap–oxidized oil titrations. A standard solution of zinc soap was prepared such that 4 ml. of solution contained 0.1 gram of zinc soap. Samples of 4 ml. of this solution were mixed with 5 grams of a typical oxidized motor oil, and titrated in each solvent-water mixture with 0.0852 *N* alcoholic potassium hydroxide.

The results of the titrations are summarized in Tables II and III, and the titration curves are shown in Figures 3 to 5. They indicate that while all solvent-water mixtures are suitable for the determination, the most desired titration characteristics are obtained using 0.5 to 2.5% water. On both sides of this range the titration curve is more dwarfed, and the characteristics of the titration are more erratic. The equilibration rate is more rapid as more and more water is added; however, the increase in rapidity is not pronounced after 0.5% water has been added. Balancing all factors such as equilibrium rate, the desire for a high water tolerance in the final medium, the desire for undwarfed titration curves, etc., the 0.5% value for water is considered optimum; it has been found very successful in routine application of the method.

Titration of Combined Acids and Bases. The same water-solvent mixtures used for the free acid-base investigation were employed for a study of the influence of water upon the combined acid-base determinations.

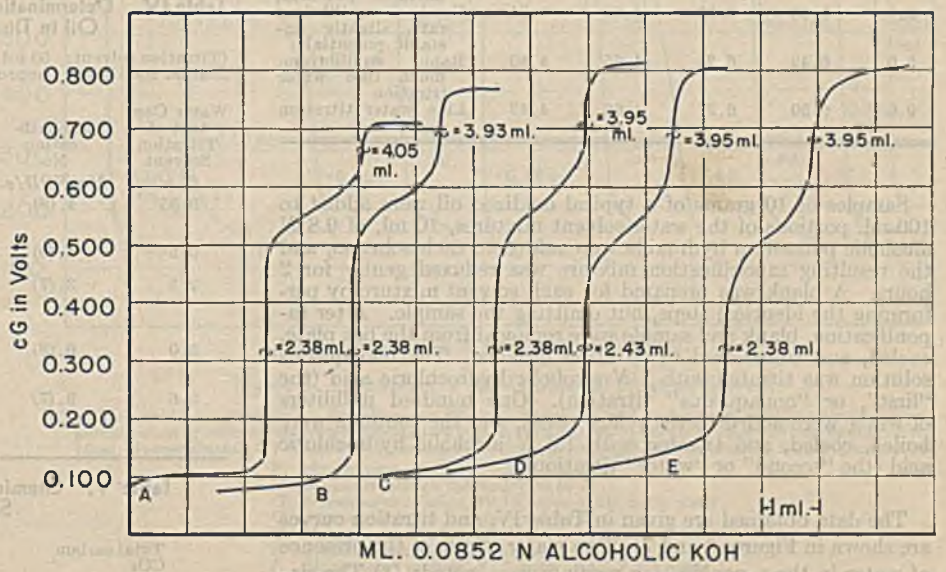

Figure 4. Optimum Water Content of Titration Solvent

Free acid-base procedure. Potentiometric titrations of mixtures of hydrochloric acid and naphthone A in titration solvent containing: *A* 0.05, *B* 0.50, *C* 2.5, *D* 5.0, and *E* 9.6% water
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol

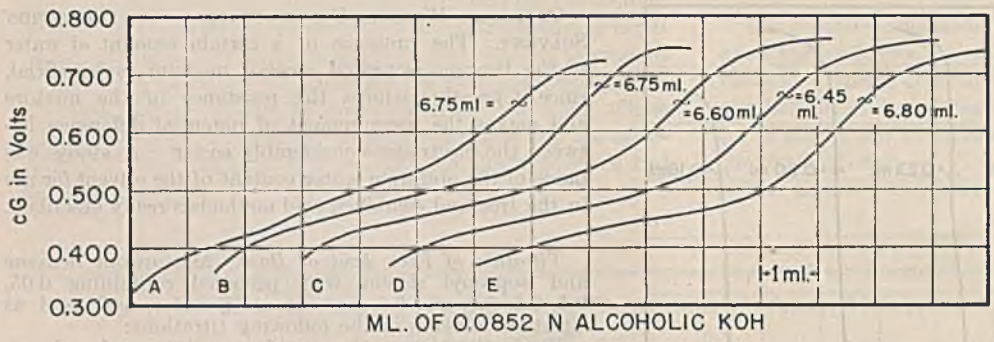

Figure 5. Optimum Water Content of Titration Solvent

Free acid-base procedure. Potentiometric titrations of 5 grams of oxidized oil and 0.100 gram of zinc soap in titration solvent containing: *A* 9.6, *B* 5.0, *C* 2.5, *D* 0.5, and *E* 0.05% water
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol

Table II. Titration of Hydrochloric Acid and Naphthone A in Titration Solvent Containing Water

(Titration solvent: 50 ml. of benzene, 50 ml. of isopropyl alcohol)

Water Content of Titration Solvent	0.0852 *N* Base					
	Solvent blank	Strong Acids Found	Strong Acids Theory	Weak Acids Found	Weak Acids Theory	Remarks
% *v.*	*Ml.*	*Ml.*	*Ml.*	*Ml.*	*Ml.*	
0.05	0.23	2.38	2.38	1.44	1.41	Slow equilibrium, poor conductivity, potential irregular
0.5	0.18	2.38	2.38	1.37	1.41	Rapid equilibrium, stable potential
2.5	0.23	2.38	2.38	1.34	1.41	Very rapid equilibrium, very stable potential
5.0	0.20	2.43	2.38	1.32	1.41	Much like 0.5% water test
9.6	0.18	2.38	2.38	1.37	1.41	Much like water titration

Table III. Titration of Oxidized Oil Sample Containing Zinc Soap in Titration Solvents Containing Water

(Titration solvent: 50 ml. of benzene, 50 ml. of isopropyl alcohol)

Water Content of Titration Solvent	Total Acid Number: Oil (5 Grams) plus Zinc Soap (0.1 Gram) At break	At $cG = 0.65$	Increase with Zinc Soap (0.1 Gram) At break	At $cG = 0.65$	Remarks
% *v.*					
0.05	6.46	6.22	4.62	4.38	Slow equilibrium, unstable potential
0.5	6.50	6.04	4.66	4.20	Slow equilibrium, especially in break, unstable potential
2.5	6.46	6.08	4.62	4.24	Good equilibrium rate, slightly unstable potential
5.0	6.49	6.24	4.65	4.40	Rapid equilibrium, much like water titration
9.6	6.50	6.27	4.66	4.43	Like water titration

Samples of 10 grams of a typical oxidized oil were added to 100-ml. portions of the water-solvent mixtures, 10 ml. of 0.8 *N* alcoholic potassium hydroxide were added to each solution, and the resulting saponification mixture was refluxed gently for 2 hours. A blank was prepared for each solvent mixture by performing the identical steps, but omitting the sample. After saponification, blank and sample were removed from the hot plate, cooled, and transferred to titration beakers. The nonaqueous solution was titrated with 1 *N* alcoholic hydrochloric acid (the "first", or "nonaqueous" titration). One hundred milliliters of water were added to the reflux vessel, and the contents were boiled, cooled, and titrated with 1.0 *N* alcoholic hydrochloric acid (the "second" or "water" titration).

The data obtained are given in Table IV, and titration curves are shown in Figures 6 and 7. Two major effects of the presence of water in the saponification medium were noted: (1) The size of the second titration increases with increasing water concentration to a maximum at 2.5% water, then decreases slightly, and (2) when more than 0.5% water is present in the medium, the salts formed during the nonaqueous titration tend to coat the electrodes and beaker walls, slowing the rate of equilibration and rendering the titrations almost impossible.

The second effect must naturally be avoided, so that a limitation of the water content to less than 0.5% is absolutely necessary. The first effect places a still greater limit on the water content. Previous to the determination of optimum water content, the possibility of determining combined acids by saponification in the benzene–isopropyl alcohol medium had been investigated. Several unsuccessful attempts were made to employ a single direct titration of the saponification mixture in the reflux vessel; in every case there was an unaccountable loss in caustic when the direct titration was employed, while no loss was noted when the double titration procedure was used. It was soon discovered in running many identical samples and blanks by both procedures, that the loss in caustic was proportional to the size of the second or water titration to be expected from the mixture. Apparently, the second titration results from the reaction of caustic with the reflux vessel or with some other substance to form a residue that is insoluble in the titration solvent but soluble in hot water. This material does not react with hydrochloric acid in the nonaqueous medium, but is readily titrated with acid in the aqueous medium. The analysis of a typical water-soluble saponification residue is given in Table V. Nothing is known concerning the nature of these residues, but the presence of water seems to promote their formation. Therefore, if a direct titration is to be used, it is necessary to maintain

Table IV. Determination of Saponification Number of an Oxidized Oil in Titration Solvent Containing Water

(Titration solvent: 50 ml. of benzene, 50 ml. of isopropyl alcohol. Saponification conditions: approximately 10 grams of oil, 7 ml. of 1.0 *N* alcoholic KOH)

Water Content of Titration Solvent	Saponification No.	Strong Acid Saponification No.	Remarks
% *v.*	*Mg. KOH/g.*	*Mg. KOH/g.*	
0.05	4.(8)	1.(2)	Very rapid equilibration, negligible second titration, ideal conditions
0.5	4.(0)	1.(0)	Rapid equilibration, second titration fairly small
2.5	3.(7)	0.(0)	Two phases on addition of caustic. Equilibration slow, potentials unsteady, second titration high
5.0	6.(8)	1.(8)	Two phases on addition of caustic, equilibration slow, second titration large
9.6	3.(7)	0.(8)	Two phases on addition of caustic, equilibration rapid, fairly small second titration

Table V. Chemical Analysis of Typical Water-Soluble Saponification Residue

	Mg.
Total carbon	1642
CO_2	29
B_2O_3	15
SiO_2	100
Total potassium (K_2O)	182
Total alkalinity (K_2O)	182

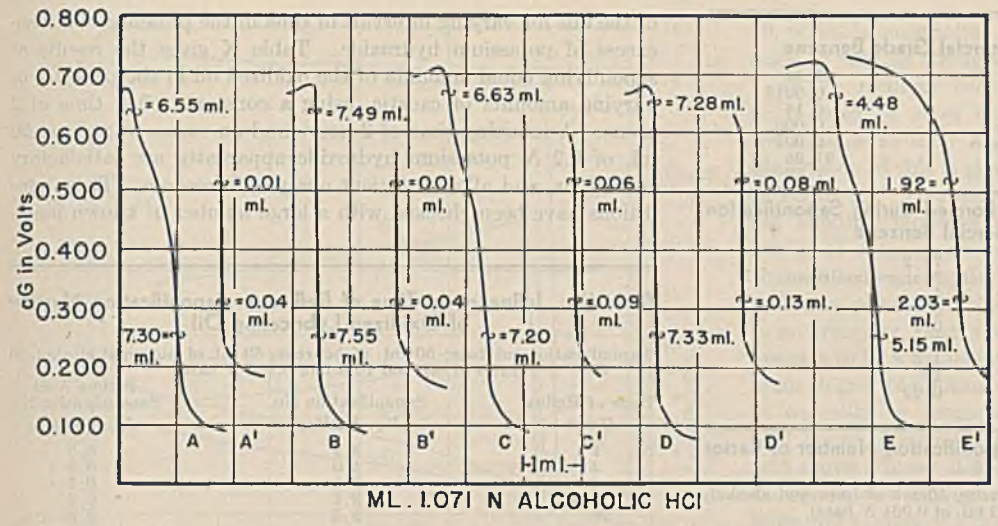

Figure 6. Optimum Water Content of Titration Solvent

Combined acid-base procedure. Potentiometric titration of aqueous and nonaqueous solutions resulting from saponification of indicated amounts of oxidized oil in presence of 50 ml. of benzene, 50 ml. of isopropyl alcohol, 10 ml. of approximately 0.7 *N* alcoholic potassium hydroxide, and indicated amounts of water; 2-hour reflux period

A. Nonaqueous solution, 11.71 grams of oil, 0.05% water
A'. Aqueous solution corresponding to *A*
B. Nonaqueous solution, blank, 0.05% water
B'. Aqueous solution corresponding to *B*
C. Nonaqueous solution, 10.18 grams of oil, 0.5% water
C'. Aqueous solution corresponding to *C*
D. Nonaqueous solution, blank, 0.5% water
D'. Aqueous solution corresponding to *D*
E. Nonaqueous solution, 10.31 grams of oil, 2.5% water
E'. Aqueous solution corresponding to *E*

a low concentration of water in the saponification medium. No difficulty is encountered if the water content is below 0.1%.

Necessary Purity of Titration Solvent. In several thousand analyses of oxidized oils, it was found that the impurities present in ordinary commercial grades of benzene and isopropyl alcohol tend to produce erratic and inaccurate results when these solvents are used in the combined acid-base procedure. Deviations of as much as 30% have been obtained using the commercial solvents. This inaccuracy, not encountered in the case of free acid-base determinations, is apparently due to the presence of difficultly saponifiable compounds of sulfur or chlorine, or of materials which tend to form resins in the presence of excess caustic.

Commercial isopropyl alcohol occasionally contains appreciable amounts of unsaturated material, aldehydes, or ketones. On standing with excess potassium hydroxide, these materials form resins which color the alcohol yellow and cause objectionably high blanks in the combined acid-base procedure. The isopropyl alcohol used should develop no color on standing with solid potassium hydroxide, should contain less than 0.1% water by test, and should have low inherent acidity.

Commercial benzene generally contains saponifiable compounds of sulfur and chlorine which react more or less completely with potassium hydroxide. Since a great many factors can influence the rate of saponification of such compounds, considerable variation is obtained in the saponification numbers determined using commercial benzene even when blank determinations are made. A typical analysis of ordinary commercial benzene is given in Table VI, and the analysis of a typical precipitate formed by reacting the benzene with potassium hydroxide in Table VII.

Ordinary commercial benzene or isopropyl alcohol can be easily purified to meet specifications by refluxing over potassium hydroxide for several hours, and then carefully fractionating.

Addition of Soluble Electrolyte to Improve Conductivity of Titration Solvent. The addition of lithium chloride to the benzene–isopropyl alcohol medium was suggested as a means of reducing the resistance of the titration solvent. Trials were made using various concentrations of lithium chloride in the medium, but it was found to react with caustic and cause a considerable error in the titration curve. To date, no soluble metallic salt has been found which is inert to potassium hydroxide in the medium. If such a salt can be found, its use may improve the characteristics of the solvent.

Characteristics of Benzene–Isopropyl Alcohol Titration Solvent. *Equilibrium Rate.* All acids, bases, and salts, are ionized in benzene–isopropyl alcohol solvent to a degree comparable with that in water. Therefore it is assumed that the reactions taking place in the free acid-base titration are very rapid. As in aqueous solutions, saponification takes place at

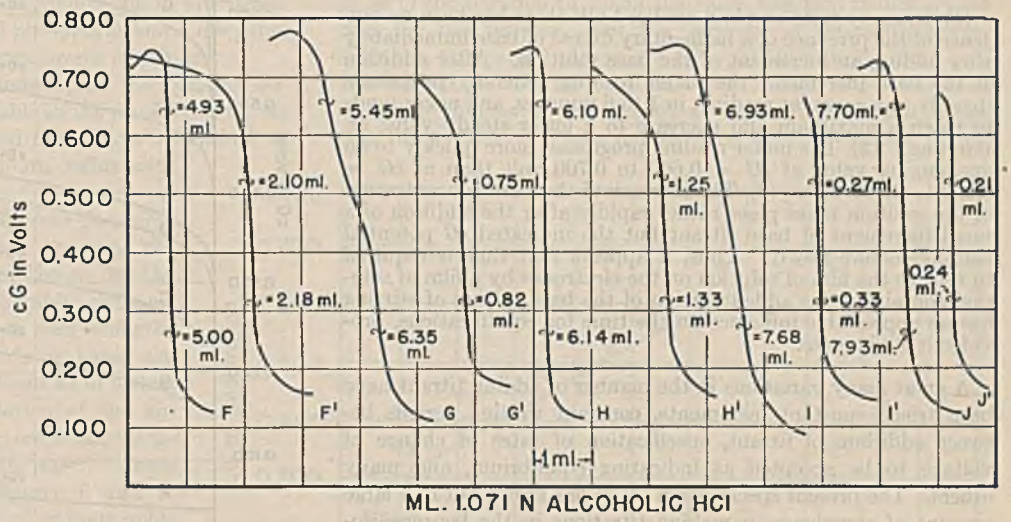

Figure 7. Optimum Water Content of Titration Solvent

Combined acid-base procedure. Potentiometric titration of aqueous and nonaqueous solutions resulting from saponification of indicated amounts of oxidized oil in presence of 50 ml. of benzene, 50 ml. of isopropyl alcohol, 10 ml. of approximately 0.7 *N* alcoholic potassium hydroxide and indicated amounts of water; 2-hour reflux period

F. Nonaqueous solution, blank, 2.5% water
F'. Aqueous solution corresponding to *F*
G. Nonaqueous solution, 10.13 grams of oil, 5.0% water
G'. Aqueous solution corresponding to *G*
H. Nonaqueous solution, blank, 5.0% water
H'. Aqueous solution corresponding to *H*
I. Nonaqueous solution, 8.15 grams of oil, 9.6% water
I'. Aqueous solution corresponding to *I*
J. Nonaqueous solution, blank, 9.6% water
J'. Aqueous solution corresponding to *J*
Titration cell. Glass electrode || calomel electrode

Table VI. Analysis of Commercial Grade Benzene

Purity by freezing point, %	99.92
Sulfur, %	0.0013
Chlorine, %	0.14
Carbonyl value, mole per 100 grams	0.006
Acetyl value, equivalent per 100 grams	0.002
Carbon, %	91.96
Hydrogen, %	7.79

Table VII. Analysis of Precipitate Formed during Saponification of Blanks Using Commercial Benzene

Sulfate ash, %	71.2
Potassium	Major constituent
Silicon, %[a]	1
Calcium, %[a]	0.1 – 1
Sodium, %[a]	0.1
Carbon, %	3.3
Hydrogen, %	1.3
Chlorine, %	23
Sulfur, %	0.09

[a] Order of magnitude only.

Table VIII. Influence of Time on Saponification Number of Castor Oil

(Saponification condition: 50 ml. of benzene, 50 ml. of isopropyl alcohol, 1.00 gram of castor oil, and 10 ml. of 0.904 *N* base)

Time of Reflux	Saponification No.	Strong Acid Saponification No.	Saponified
Min.	*Mg. KOH/g.*	*Mg. KOH/g.*	%
0	118	0.0	65
5	155	1.0	86
15	165	3.0	91
30	175	1.0	97
60	181	1.0	100
60[a]	186	3.0	...
420[a]	194	0.0	...

[a] Sample and blank contained 10 grams of SAE 30 lubricating oil.

slow reaction rates which must be taken into consideration in determining the time of reflux necessary for the saponification of combined acids and bases, and in estimating the necessary excess of caustic to saponify combined acids and bases in a reasonable length of time. Unlike titrations in aqueous media, titration in benzene–isopropyl alcohol solution requires that considerable time be allowed between increments of titrant to allow the electrode potential to come to reasonable equilibrium.

The course of events as each drop of titrant is added during a titration is indicated by the following observations.

(1) In many tests on plain oxidized oils there has been no evidence of the presence of a momentary excess of base immediately after adding an increment of the base solution. After addition of the base increment, the meter reading generally progresses steadily to a constant reading, in 1 to 6 minutes, and never tends to reach a maximum and decrease to a lower steady value on standing. (2) The meter reading progresses more quickly to an unchanging value at cG = 0.600 to 0.700 volt than at cG = 0.400 to 0.500 volt. (3) The increase of the base concentration of the solution takes place rather rapidly after the addition of a small increment of base titrant but the indicated cG potential reading follows slowly. Thus, it appears that time is required to replace the film of solution on the electrodes by a film of solution containing the added portion of the base. Rate of stirring has no appreciable influence on the time for equilibrations, provided it is adequate.

A great many variations in the manner of adding titrant have been tried—constant increments, constant waiting periods between additions of titrant, specification of rates of change of voltage to be accepted as indicating equilibrium, and many others. The present specification (*1, 2*) has grown out of a large amount of experience in making titrations in the benzene–isopropyl alcohol medium. It has been applied with success to a large number of standard samples in which the acid and basic strengths have varied from the highest to the lowest detectable by the method.

Reaction of Caustic with Combined Acids and Bases in the Medium. The excess of potassium hydroxide, and the time of reflux necessary for complete saponification of combined acids and bases, were experimentally determined using a sample of pure castor oil and a typical sample of oxidized oil. Tables VIII and IX summarize the results of saponifying equal amounts of the oils for varying intervals of time in the presence of a large excess of potassium hydroxide. Table X gives the results of saponifying equal amounts of the oxidized oil in the presence of varying amounts of caustic, using a constant reflux time of 2 hours. A refluxing time of 2 hours and an excess of at least 20 ml. of 0.2 *N* potassium hydroxide apparently are satisfactory conditions, and allow sufficient analytical freedom. These conditions have been checked with a large number of known mate-

Table IX. Influence of Time of Reflux on Saponification Number of Oxidized Lubricating Oil

(Saponification mixture: 50 ml. of benzene, 50 ml. of isopropyl alcohol, 10 grams of oil, and 10 ml. of 0.904 *N* base)

Time of Reflux	Saponification No.	Strong Acid Saponification No.
Hours	*Mg. KOH/g.*	*Mg. KOH/g.*
1	3.9	0.9
2	4.0	0.8
4	3.5	0.7
7.5	3.1	0.7
20	3.5	0.6

Table X. Influence of Excess Caustic upon Saponification Number of a Used Lubricating Oil

(Saponification condition: 50 ml. of benzene, 50 ml. of isopropyl alcohol 10 grams of oil, and 2 hours' reflux)

0.904 *N* Alcoholic KOH in Medium	Saponification No.	Strong Acid Saponification No.
Ml.	*Mg. KOH/g.*	*Mg. KOH/g.*
1.00	4.1	0.9
3.00	6.4	1.8
5.00	6.9	2.0
7.00	7.5	2.4
9.00	8.0	3.3
10.00	7.7	2.9

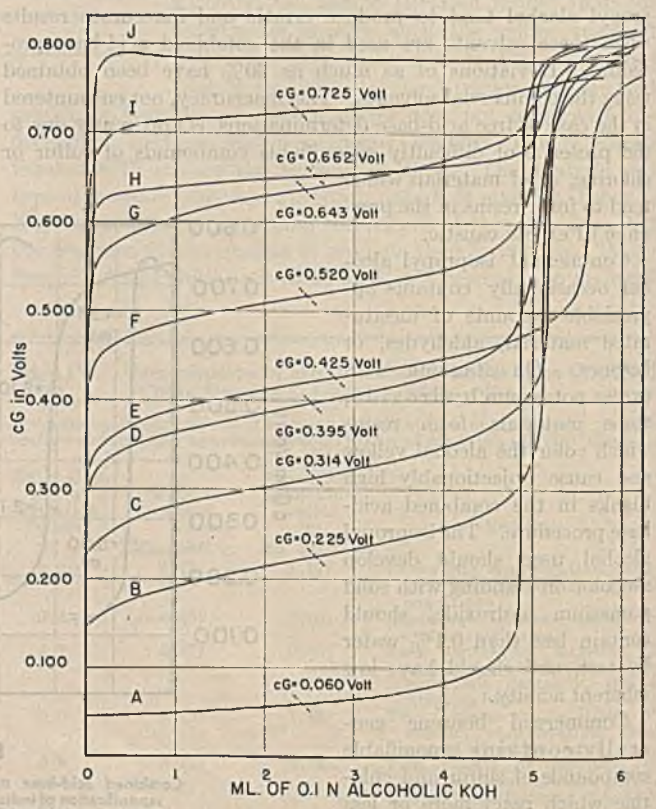

Figure 8. Influence of Acid Strength upon Free Acid Titration Curve

Potentiometric titration of acids with alcoholic potassium hydroxide:

A. Hydrochloric acid
B. Trichloroacetic acid
C. Dichloroacetic acid
D. Monochloroacetic acid
E. Formic acid
F. Acetic acid
G. *p*-Nitrophenol
H. *m*-Nitrophenol
I. Phenol (hydroxybenzene)
J. Blank

Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

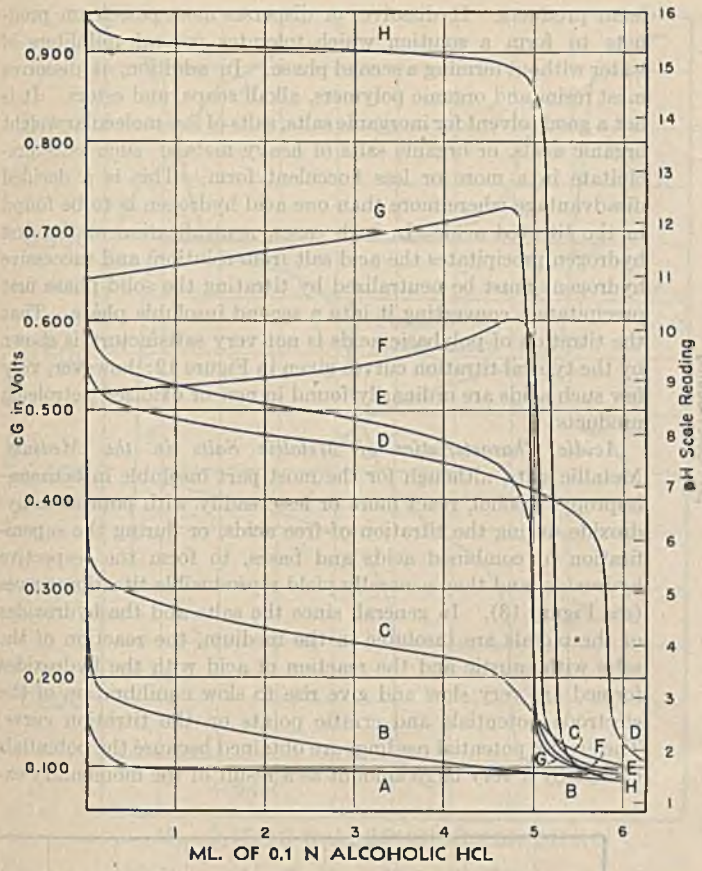

Figure 9. Influence of Base Strength upon Free Base Titration Curve

Potentiometric titration of bases with alcoholic hydrochloric acid:

A. Blank
B. Pyridine
C. Hexamethylenetetramine
D. Ammonia
E. Butylamine
F. Sodium hydroxide
G. Potassium hydroxide
H. Tetraethylammonium hydroxide

Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

rials and found to produce complete saponification in practically all the trials. Certain compounds of phosphorus and a few other inert organic substances required more severe conditions.

Throughout these tests, it was found that the benzene–isopropyl alcohol titration solvent is stable in the presence of excess base. It is not appreciably attacked even under conditions of drastic saponification, such as 48 hours' reflux with excess strong base.

Ionization of Acids and Bases in Benzene–Isopropyl Alcohol Titration Solvent. While the apparent degree of ionization of most acids and bases in the benzene–isopropyl alcohol is measurably different from that in water, the relative acid or base strengths of the members of a series of acids or bases are in the same order in this titration solvent as in water; however, there is a better differentiation of the apparent degree of ionization of the more acidic materials in this titration solvent than in water. These relationships are illustrated by Figures 8 and 9, which give typical titration curves of various acids and bases titrated in the benzene–isopropyl alcohol titration solvent. Since it is assumed that the *cG* potential is a measure of the hydrogen activity of a nonaqueous solution, it is further assumed that the *cG* potential at the mid-titration indicates the relative acid or base strength of the substance in this titration solvent. That there is a definite relationship between this *cG* mid-titration point in benzene–isopropyl alcohol medium and the pK_a value in water is indicated by the smooth curve given in Figure 10, which is constructed by plotting these values for typical acids of varying strengths.

As the medium becomes less and less waterlike, strong acids tend to show considerably more irregularity than weak acids in their apparent degrees of ionization. An illustration of this is given by the family of titration curves in Figure 11. This series of curves was prepared by titrating identical mixtures of strong acids and weak acids in media of successively less waterlike properties. Evidently there is a large regular departure in the position of the buffering plateau in the case of the weak acid in contrast to an irregular change in that of the strong acid. There appears to be a tendency for the strong acid to show a maximum degree of ionization in solvents that are intermediate in waterlike or nonaqueous properties, while the weak acid shows a regular trend in this respect—that is, a weak acid shows a lower degree of ionization and a strong acid shows a somewhat higher degree of ionization in benzene–isopropyl alcohol medium than in water. Practically, this means that when using the benzene–isopropyl alcohol titration solvent there is a better chance of distinguishing between acids whose pK_a (H_2O) are in the range of 1 to 3 than between those whose pK_a (H_2O) range from 6 to 8.

Titration Curves for Oxidized Oils. The acidity or basicity present in oxidized oils is by no means necessarily due to a single acid or base. It may be and probably is made up of a large number of different components, each having its own individual degree of ionization. As a result, in contrast to the clear titration curves produced by single acids or bases (Figures 8 and 9), the oxidized oils yield indefinite titration curves of the type illustrated by curves *B* and *E* of Figure 1 and *B* of Figure 2. In most cases there is an inflection on the curve to indicate the end point; however, in some instances, the titration curves exhibit no recognizable inflection. In such cases, in order to measure the changes of acidity or basicity taking place during the oxidation of the oil, it is necessary to establish definite *cG* reference points to be used to indicate the end point of the titration in much the same way that indicators are used for this purpose. For the purposes of the methods presented in this paper, the points *cG* = 0.650 volt for total acid and *cG* = 0.236 volt for total base were chosen to represent the end point indicating the transition to strong base and strong acid, respectively. These points were selected because for all

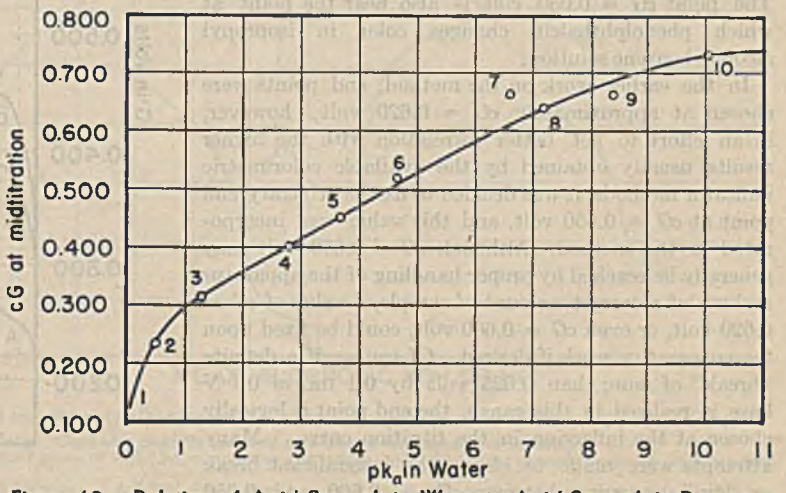

Figure 10. Relation of Acid Strength in Water to Acid Strength in Benzene–Isopropyl Alcohol Titration Solvent

1. Hydrochloric acid
2. Trichloroacetic acid
3. Dichloroacetic acid
4. Monochloroacetic acid
5. Formic acid
6. Acetic acid
7. Thiophenol
8. *p*-Nitrophenol
9. *m*-Nitrophenol
10. Phenol

Based on titration curves shown in Figure 8

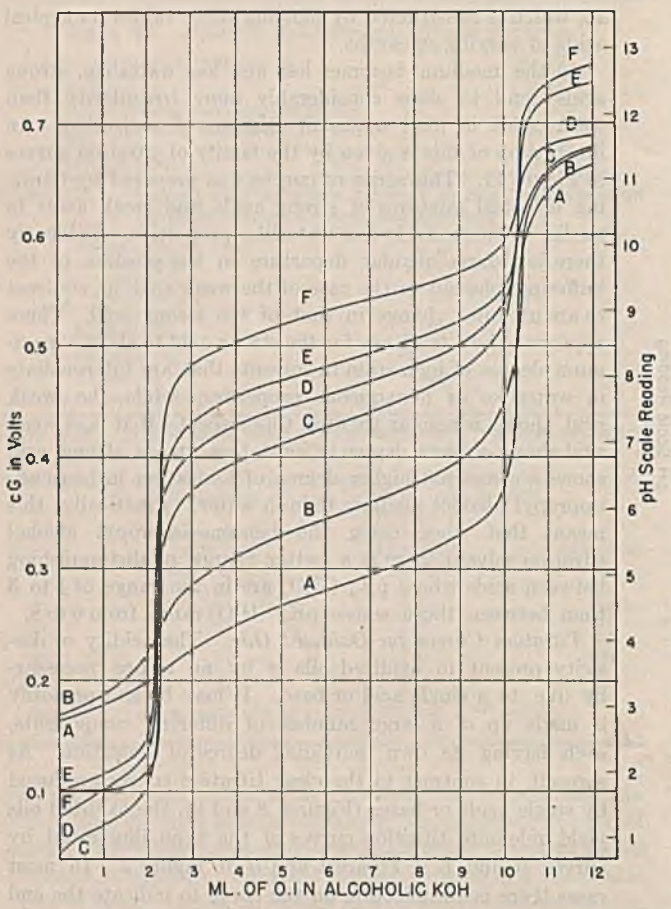

Figure 11. Effects of Nonaqueous Medium Characteristics upon Free Acid Titration Curves

Potentiometric titration of hydrochloric and acetic acids with alcoholic potassium hydroxide in the following media:
A. 125 ml. of water
B. 62 ml. of methanol, 62 ml. of water
C. 125 ml. of methanol (0.5% water)
D. 125 ml. of ethanol (0.5% water)
E. 125 ml. of isopropyl alcohol (0.5%) water
F. 62 ml. of benzene, 62 ml. of isopropyl alcohol containing 1% water
Titration cell. Glass electrode || calomel electrode

samples that give good inflections in the titration curves, the inflections occurred at or near these points. The point $cG = 0.650$ volt is also near the point at which phenolphthalein changes color in isopropyl alcohol–benzene solution.

In the earlier work on the method, end points were chosen at approximately $cG = 0.620$ volt; however, in an effort to get better correlation with the higher results usually obtained by the available colorimetric indicator methods, it was decided to fix the arbitrary end point at $cG = 0.650$ volt, and this value was incorporated in the method. Although $cG = 0.650$ volt may generally be reached by proper handling of the apparatus and use of a correct amount of sample, a value of $cG = 0.620$ volt, or even $cG = 0.600$ volt, could be fixed upon for cooperative work if desired. Of course, if a definite "break" of more than 0.025 volt by 0.1 ml. of 0.1 N base is realized in this range, the end point is logically chosen at the inflection in the titration curve. Many attempts were made to choose the insignificant break or "dip" occurring between $cG = 0.600$ and 0.650 volt, which is often found with oxidized oils, but precision was generally poor and erratic and this practice was abandoned.

Solvent Action. The benzene–isopropyl alcohol titration solvent is a very good solvent for practically all petroleum products. It dissolves or disperses most petroleum products to form a solution which tolerates several milliliters of water without forming a second phase. In addition, it dissolves most resins and organic polymers, alkali soaps, and esters. It is not a good solvent for inorganic salts, salts of low molecular weight organic acids, or organic salts of heavy metals; such salts precipitate in a more or less flocculent form. This is a decided disadvantage where more than one acid hydrogen is to be found in the titrated acid. In such cases, neutralization of the first hydrogen precipitates the acid salt from solution, and successive hydrogens must be neutralized by titrating the solid phase first precipitated, converting it into a second insoluble phase. That the titration of polybasic acids is not very satisfactory is shown by the typical titration curves given in Figure 12; however, very few such acids are ordinarily found in new or oxidized petroleum products.

Acidic Characteristics of Metallic Salts in the Medium. Metallic salts, although for the most part insoluble in benzene–isopropyl alcohol, react more or less readily with potassium hydroxide during the titration of free acids, or during the saponification of combined acids and bases, to form the respective hydroxide, and they generally yield reproducible titration curves (see Figure 13). In general, since the salts and the hydroxides of the metals are insoluble in the medium, the reaction of the salts with caustic and the reaction of acid with the hydroxides formed are very slow and give rise to slow equilibration of the electrode potentials and erratic points on the titration curve. The erratic potential readings are obtained because the potentials change by a very large amount as a result of the momentary ex-

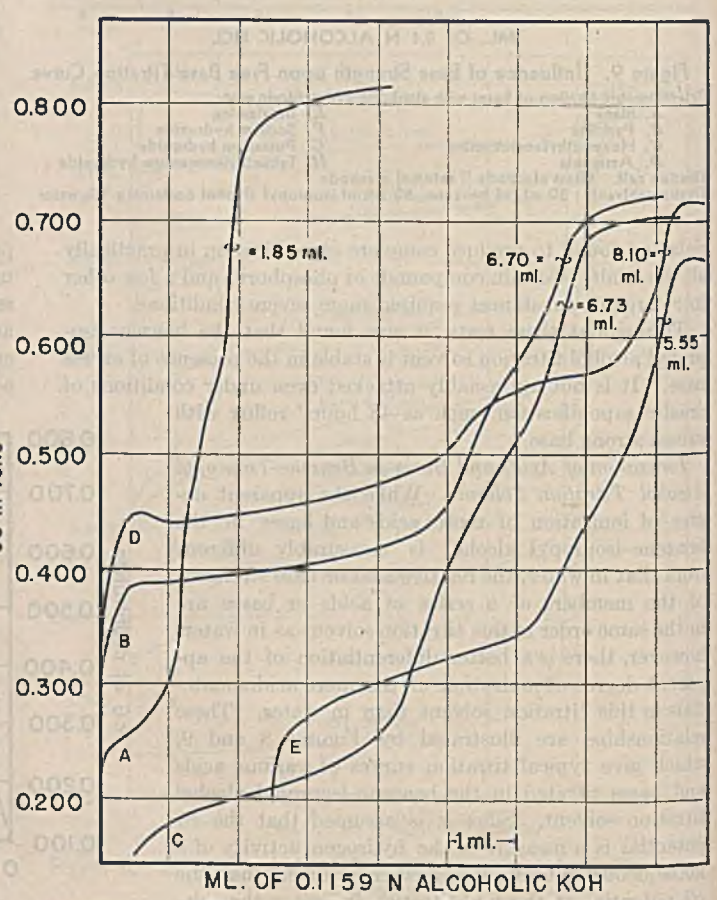

Figure 12. Titration of Polybasic Acids

Potentiometric titration of polybasic acids with alcoholic potassium hydroxide:
A. 2.0 ml. of 0.1907 N aqueous phosphoric acid. Theoretical total titration, 3.29 ml
B. 0.055 gram of succinic acid. Theoretical total titration, 8.20 ml.
C. 0.054 gram of maleic acid. Theoretical total titration, 8.20 ml.
D. 0.094 gram of sebacic acid. Theoretical total titration, 8.15 ml.
E. 0.077 gram of *o*-phthalic acid. Theoretical total titration, 8.15 ml.
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

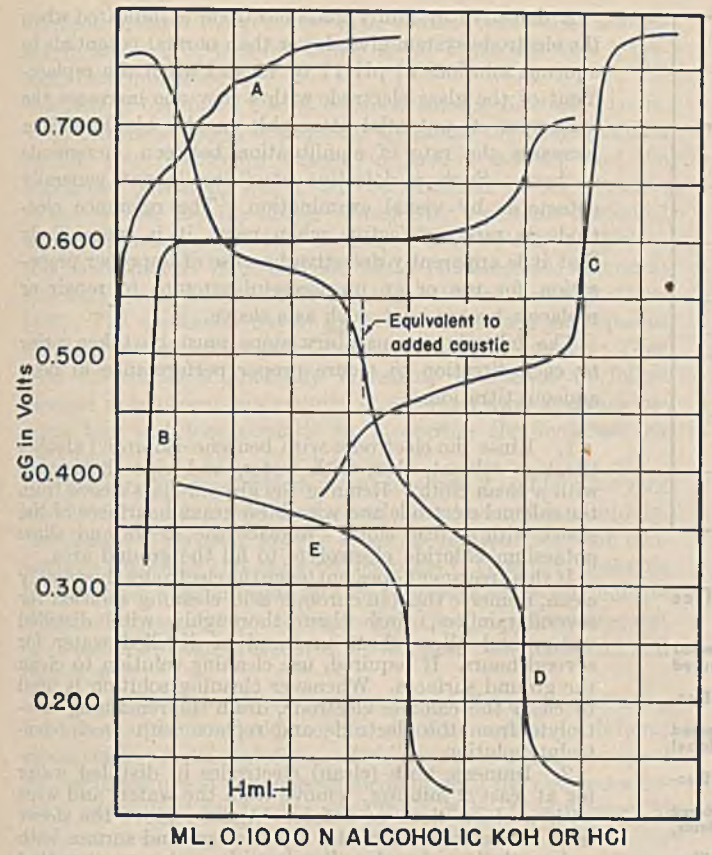

Figure 13. Titration of Metallic Salts

Potentiometric titration with alcoholic potassium hydroxide:
A. 0.1172 gram of copper palmitate *C*. 0.1170 gram of zinc soap
B. 0.0276 gram of lithium chloride
Potentiometric titration with alcoholic hydrochloric acid:
D. 0.10 gram of calcium soap, saponified with 40 ml. of 0.2 *N* alcoholic potassium hydroxide (combined acid-base procedure). *E*. 0.1000 gram of zinc soap
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

cess produced by each increment of titrant, and then fade slowly back to the normal potential as the excess is slowly reduced by the reaction. This behavior not only causes error in estimation of the free or combined organic acids, but also prolongs the titration to an impractical point.

In an attempt to overcome this metal salt interference, sodium oxalate was added to the medium before the titration, in the hope that the sodium oxalate would precipitate the heavy metals as oxalates, leaving the nonreacting sodium salts in their place. However, use of the oxalate did not reduce the interference by the metal salts and in some cases a considerably greater error resulted from its use. No attempt was made to find a more suitable anion than the oxalate ion.

APPARATUS

Although most glass electrode and meter assemblies intended for pH determination function satisfactorily in an aqueous medium, many are not directly applicable for similar measurements in a nonaqueous medium. Although not all the exact specification limits have been established, satisfactory results are obtainable by the proposed method when the electrodes and meter possess certain essential characteristics which are noted below.

ELECTRODES. *Selection of Electrode System.* Most of the electrodes suggested in the literature were experimentally evaluated for the measurement of hydrogen-ion activity and for use as reference electrodes. The principal electrodes tried are listed above; their faults were verified by experiment.

A considerable number of reference electrodes were tried, most of them differing only in the type of salt bridge. Many variations of the salt bridge were applied, including the use of various organic electrolyte media. The best all-around reference electrode was found to be a saturated calomel (aqueous) half-cell with a ground-glass contact. Of several reference electrodes tried, the only one that gave suitable service was the Beckman No. 4970A calomel electrode having a ground-glass sleeve. This is a pencil-type electrode having a permanent inner cell surrounded by potassium chloride solution. Contact between the electrolyte solution and titration medium is made by a removable ground-glass sleeve.

The only electrodes which were found suitable for use as hydrogen-ion indicating electrodes in nonaqueous media were the thin (low-resistance) glass electrode and the modern sturdy (high-resistance) glass electrode; the former was discarded because of its extreme fragility. All-glass electrodes of the sturdy type available from American manufacturers were tested for use in the benzene–isopropyl alcohol titration solvent. The only ones found suitable were the Beckman No. 4990 and No. 4990E electrodes. All others (including the Beckman No. 4990X electrode) failed in some respect to give satisfactory results or service. The No. 4990 electrode is 12.5 cm. (5 inches) long with a diameter of 1.445 cm. (0.578 inch) and a bulb of Corning 015

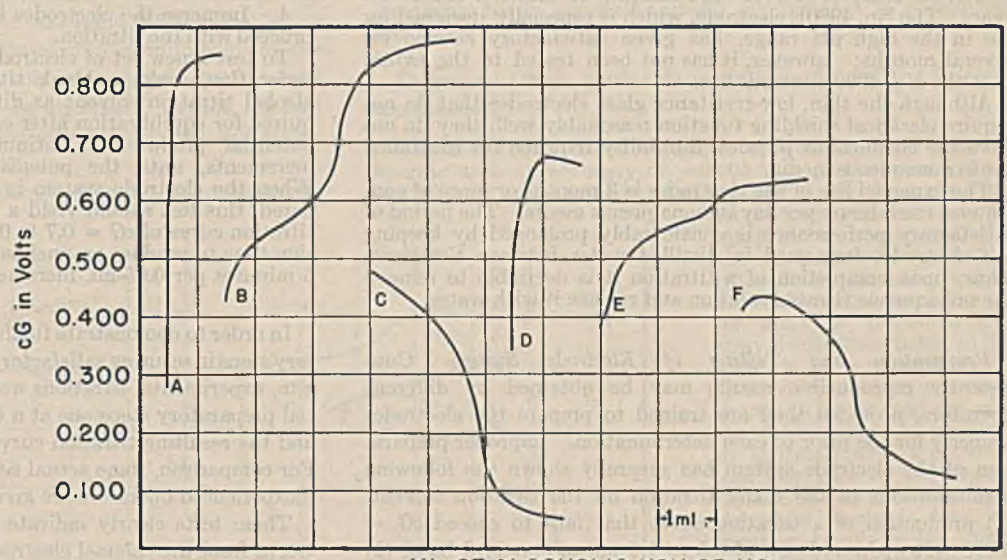

Figure 14. Effect of Improper Maintenance of Electrodes upon Free Acid-Base Titration Curves

A. Titration for free acid in blank. Electrodes carefully prepared according to directions given in method
B. Titration for free acid in 4.99 grams of A.S.T.M. cooperative test sample N-8. Electrodes properly prepared according to method
C. Titration for free base in 5.06 grams of A.S.T.M. cooperative test sample N-4. Electrodes properly prepared according to method
D. Titration for free acid in blank. Electrodes treated in recommended manner after making titration *C*, but not allowed to soak 2 minutes in distilled water before titrating
E. Titration for free acid in 5.00 grams of A.S.T.M. cooperative test sample N-8. Electrodes treated in recommended manner, but not allowed to soak 2 minutes in distilled water before titrating
F. Titration for free base in 5.04 grams of A.S.T.M. sample N-4. Electrodes treated in recommended manner, but not allowed to soak 2 minutes in distilled water before titrating
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

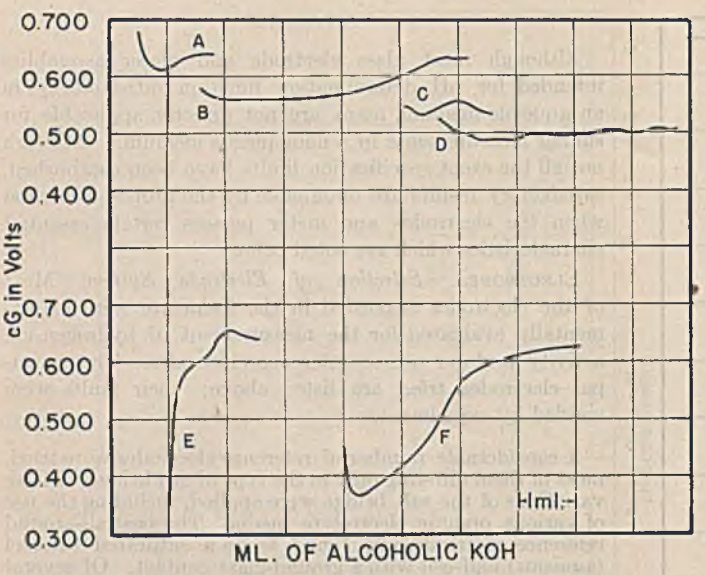

Figure 15. Effect of Improper Maintenance of Electrodes upon Free Acid-Base Titration Curves

A. Titration of free acid in blank. Electrodes, following nonaqueous titration, washed down with benzene–isopropyl alcohol only, calomel electrode sleeve not removed before titrating
B. Titration of free acid in 5.05 grams of A.S.T.M. cooperative test sample N-7. Electrodes prepared as in *A*
C. Titration of free acid in blank. Electrodes, following nonaqueous titration, washed down with benzene–isopropyl alcohol only, and wiped dry. Sleeve of calomel electrode removed, wiped dry, and replaced in recommended manner
D. Titration of free acid in 5.02 grams of A.S.T.M. cooperative test sample N-5. Electrodes prepared as in *C*
E. Titration of free acid in blank. Electrodes, following nonaqueous titration, rinsed with isopropyl alcohol–benzene, then with water. Immersed in water, for 0.5 minute, then dried. Calomel electrode sleeve not removed prior to titration
F. Titration of free acid in 5.00 grams of A.S.T.M. cooperative test sample N-5. Electrodes prepared as in *E*
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

glass; it has a resistance of 200 to 300 megohms at room temperature. This type of electrode has been used with good success in the analysis of over 5000 samples of oxidized oils over 3 years. The No. 4990E electrode, which is especially designed for use in the high pH range, has given satisfactory service for several months; however, it has not been tested to the extent that the No. 4990 electrode has.

Although the thin, low-resistance glass electrodes that do not require electrical shielding function reasonably well, they do not have the chemical or physical durability required for continued use in nonaqueous media.

The expected life of the electrodes is 3 months or more of continuous use 8 hours per day in nonaqueous media. The period of satisfactory performance is considerably prolonged by keeping the electrodes immersed in distilled water between titrations. Thus, upon completion of a titration it is desirable to remove the nonaqueous titrated solution and replace it with water.

Preparation and Testing of Electrode System. Consistently reproducible results may be obtained by different operators, provided they are trained to prepare the electrodes properly for use prior to each determination. Improper preparation of the electrode system has generally shown the following manifestations in the blank titration on the titration solvent: (1) production of a titration curve that fails to exceed cG = 0.700 volt upon addition of 0.5 to 1.0 ml. of standard base, (2) extremely slow rate of equilibration between increments of base, (3) little or no change in potentials with the initial increments of base, and (4) tendency for the titration curve to begin at too high cG potentials. In addition, improper electrode preparation is indicated during the titration of a sample whenever the initial increments of base cause the cG potentials to decrease instead of increase. Although the glass electrode may be partially at fault, this improper performance is usually caused by the condition of the interface between the salt solution in the calomel electrode and the titration solvent.

A defective or faulty glass electrode is indicated when the electrode system gives lower than normal potentials in aqueous solutions at pH 11 to 12 and when the replacement of the glass electrode with a new one increases the maximum cG potential attainable in the blank and/or increases the rate of equilibration between increments of base. Such a defective condition is not generally detectable by visual examination. The reference electrode is rarely defective when new; it is more likely that it is apparently defective because of improper preparation for use or an unsuccessful attempt to repair or replace a broken part, such as a sleeve.

The following preparatory steps must be taken prior to each titration to secure proper performance in nonaqueous titration.

1. Rinse the electrodes with benzene–isopropyl alcohol titration solvent, then with water, and wipe thoroughly with a clean cloth. Remove the ground-glass sleeve from the calomel electrode and wipe both ground surfaces of the sleeve with a clean cloth. Replace the sleeve and allow potassium chloride electrolyte to fill the ground area.

If this treatment does not leave the electrodes thoroughly clean, immerse them in chromic acid cleaning solution for several minutes, rinse them thoroughly with distilled water, and allow them to stand in distilled water for several hours. If required, use cleaning solution to clean the ground surfaces. Whenever cleaning solution is used to clean the calomel electrode, drain the remaining electrolyte from the electrode and replace with fresh electrolyte solution.

2. Immerse both (clean) electrodes in distilled water for at least 2 minutes, remove from the water, and wipe with a clean cloth as before. Again remove the sleeve from the calomel electrode, dry each ground surface with a clean cloth, and replace the sleeve in such a manner that the ground surfaces are completely and copiously wetted with electrolyte solution. Be certain to leave a ring of electrolyte solution in the capillary space above and below the sleeve, so that good electrical contact is established at the electrolyte–titration solvent interface.

3. At all times, maintain the level of the electrolyte solution in the calomel electrode above the point to which the electrode is immersed in the titration solvent or other medium.

4. Immerse the electrodes in the solution to be titrated and proceed with the titration.

To test a new set of electrodes, or an old set suspected of deterioration, make a blank titration of the benzene–isopropyl alcohol titration solvent as directed (*1*). Record the time required for equilibration after each increment as well as the final potential produced. Continue the titration, using 0.05-ml. increments, until the potential reaches its maximum value. When the electrode system is in good order and properly prepared, this test should yield a maximum potential on the blank titration curve of cG = 0.7 to 0.8 volt and the average equilibration time to produce an unchanging potential should be less than 5 minutes per 0.05-ml. increment of base added.

In order to demonstrate further the importance of the preparatory steps in securing satisfactory performance of the electrode system, experimental titrations were made after omitting the essential preparatory steps one at a time. The conditions of the tests and the resulting titration curves are given in Figures 14 and 15. For comparison, some actual titration curves obtained by typical inexperienced operators are given in Figure 16.

These tests clearly indicate the importance of removing the sleeve from the calomel electrode and immersing both electrodes in water prior to every titration in benzene–isopropyl alcohol titration solvent. The elimination of these steps causes serious distortion of the titration curve. Apparently a water film adheres to the surface of the glass electrode for the duration of the titration and as long as this film is unbroken it provides the necessary conditions for equilibrium. Prolonged contact with the nonaqueous solvent (more than 90 minutes) tends to inactivate the electrode system, possibly by removing the water at points of contact. However, this does no permanent harm because contact with water during the preparation for the next

titration restores the activity. The contact with water also removes any caustic film remaining on the electrodes from a previous determination.

Effects of Continued Use on Characteristics of Electrode System. With continued use in nonaqueous solutions, the characteristics of the glass electrodes change in such a manner that the maximum potential, which can be obtained in the presence of excess base, steadily drops. Thus, after 6 months' continued use, the maximum potential obtainable may be only equivalent to a calculated *cG* value of 0.600 volt. This electrode deterioration is in accord with the corroborating evidence found by others (*10*). The continued use of glass electrodes in a nonaqueous titration solvent alters their characteristics in two ways: They tend to exhibit a gradually increasing reluctance to follow changes in hydrogen-ion activity in a normal way, and they become less and less accurate in measuring the hydrogen-ion activity.

When a new glass electrode is put into use, it equilibrates very rapidly for the first few weeks, and then less and less rapidly. Eventually it becomes so slow as to be unsatisfactory for nonaqueous titrations and must be discarded. Thus it is desirable to have a test of equilibrium rate for electrodes which will indicate their usefulness. Such a test is included in the performance test of electrodes in the procedures for free and combined acid and base (*1, 2*).

All glass electrodes show a certain amount of error in measuring the pH of aqueous solutions or the *cG* of nonaqueous solutions, especially in alkaline solutions. This error is gradually increased by continued use in nonaqueous medium until the electrodes become impractical for further use (Table XI). It is because of such errors in measurements by the glass electrode that no two electrode systems will give identical *cG* readings for a given solution of partially neutralized acids or bases in nonaqueous solution. Thus, some means must be used to apply a correction to the electrodes in order to determine accurately the important reference potentials, $cG = 0.236$ and 0.650 volt. This correction is determined by testing with standard nonaqueous buffers (*2*) whose *cG* readings on the basis of tests with ideal electrodes are assumed to be standard for $cG = 0.236$ and 0.650 volt. When the errors become so great that the electrodes will not reach the calculated value for $cG = 0.650$ volt in the presence of a slight excess of strong base, they must be discarded; in fact, for best results the electrodes should be discarded if they will not give a higher reading than $cG = 0.700$ volt.

The continued use of the calomel electrode in nonaqueous solutions has no apparent effect upon its useful characteristics. If proper care is exercised in its preparation and maintenance, it should last indefinitely.

Table XI. Comparison of New and Used Glass Electrodes

(Calomel electrode used as reference)

Test	New Glass Electrode	Average Glass Electrode	Borderline Glass Electrode	Unsatisfactory Glass Electrode
pH reading in pH 4.00 buffer	4.00	4.00	4.00	4.00
pH reading in pH 7.00 buffer	7.02	7.03	7.05	7.05
pH reading in pH 10.00 buffer	9.95	9.79	9.28	8.83
pH reading in pH 11.00 buffer	10.76	10.53	10.03	9.37
Maximum *cG* reading reached in free acid number blank, volt	0.796	0.742	0.720	0.692
Time required to attain maximum potential when immersed in benzene–isopropyl alcohol containing excess caustic, min.	1	2.5	7	15
cG reading in *cG* = 0.650 volt nonaqueous buffer solution, volt	0.649	0.629	0.617	0.608

TITRATION METER. Several commercial electronic voltmeters were tested for applicability to the measurement of the voltages between the glass–calomel electrodes in the isopropyl alcohol–benzene medium.

The most satisfactory meters were the Beckman Model M (or Model O) pH meters manufactured by the National Technical Laboratories, the electronic voltmeter of equivalent characteristics (*26*), and the dual alternating current titrometer described by Penther and Rolfson (*25*). Except for the Beckman meters and electrodes, none of the commercial apparatus tested was applicable without modification to titrations in the benzene–isopropyl alcohol titration solvent, although all were applicable to titrations in an aqueous medium. In some cases, substitution of the Beckman calomel electrode for the reference electrode, furnished by the manufacturer, converted an unsatisfactory apparatus to an apparatus useful for titration in nonaqueous media.

In general terms, a suitable meter should meet the following specifications:

The meter must be a voltmeter or potentiometer that will operate with an accuracy of ±0.005 volt and a sensitivity of ±0.002 volt, over a range of at least ±0.5 volt, when used with an electrode system having 500 megohms' resistance and when the resistance between the electrodes falls within the range of 0.2 to 20 megohms. The meter must be protected from stray electrostatic fields, so that when it is connected to the electrode system no permanent change in meter readings, over the entire range, is produced by touching with a grounded lead any part of the exposed surface of the glass electrode, the glass electrode lead, the titration stand, or the meter. A satisfactory meter should be designed to operate on an input of less than 5×10^{-12} ampere when an electrode system of 1000 megohms' resistance is connected to the terminals and should be provided with a satisfactory terminal (*26*) to connect the shielded connection wire from the glass electrode to the meter without interference from the presence of external electrostatic fields.

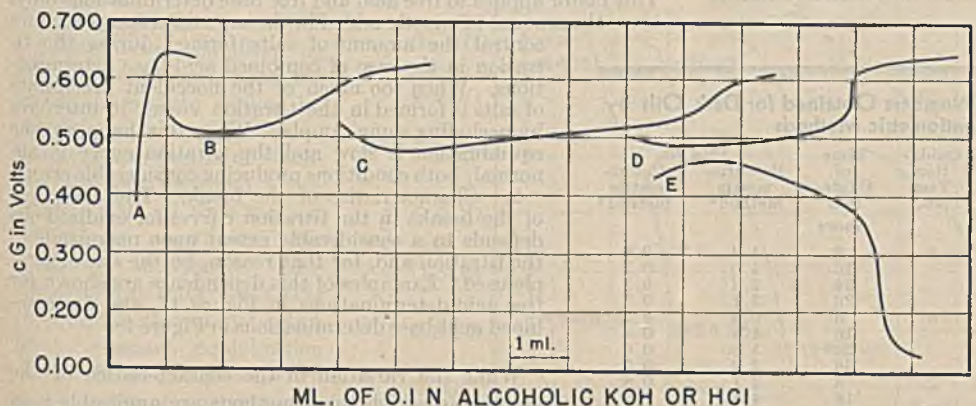

Figure 16. Free Acid-Base Titration Curves Obtained by Typical Inexperienced Operator

Potentiometric determinations of free acid by titration with alcoholic potassium hydroxide:
A. Blank
B. 10 grams of A.S.T.M. cooperative sample N-5
C. 10 grams of A.S.T.M. cooperative sample N-7
D. 10 grams of A.S.T.M. cooperative sample N-8
Potentiometric determination of free base by titration with alcoholic hydrochloric acid
E. 10 grams of A.S.T.M. cooperative sample N-4
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

Titration Stand. For most effective application of the methods given in this paper, it is necessary to have some convenient manner of mounting the electrodes, stirrer, burets, and titration beakers in a compact unit, so that cleaning, adjusting, and replacing solutions can be done with a minimum of effort and the titrations can be made conveniently and rapidly. A stand (*1*, *2*) was developed especially for this application and has been found very efficient. It is now available from a commercial supply house.

Saponification Apparatus. The greater part of the investigation of the combined acid-base determination was done using the conventional type of reflux apparatus with Erlenmeyer flask and Allihn condenser. When the properties of the solvent became better understood and the single titration procedure became possible, a special saponification reflux apparatus was devised for carrying out the saponification directly in the titration beaker (*2*); this apparatus was constructed by fitting the titration beaker with an immersion-type condenser.

Discussion

During this investigation many attempts were made to apply indicator methods to the determination of acidity in dark petroleum products for the very practical reasons of economy in time and equipment. All indicators and mixed indicators recommended in the available literature were tested, but were rejected, because the color change could not be seen in dark samples, took place too early or too late as compared with potentiometric titration results, or was gradual or indistinct. Spotlights, ultraviolet lights to induce fluorescence, white porcelain spatulas pressed against the sides of the titration flask, and tilting the flask were tried to obtain better observation of the end point, but without success.

No usable relationship has been found between acid numbers of dark oils obtained by the potentiometric method, and those obtained by the usual colorimetric methods. This is illustrated in Table XII, which shows the acid numbers obtained for several typical series of oxidized oils chosen at random from the results of a large number of oil oxidation tests. For combined acid (saponification) number, the agreement between the results of colorimetric and potentiometric methods is somewhat better (Table XIII).

Early in the development of the methods for free acid and free base, it became apparent that the slow addition of titrant could cause a gradual saponification of easily saponified materials during the titration.

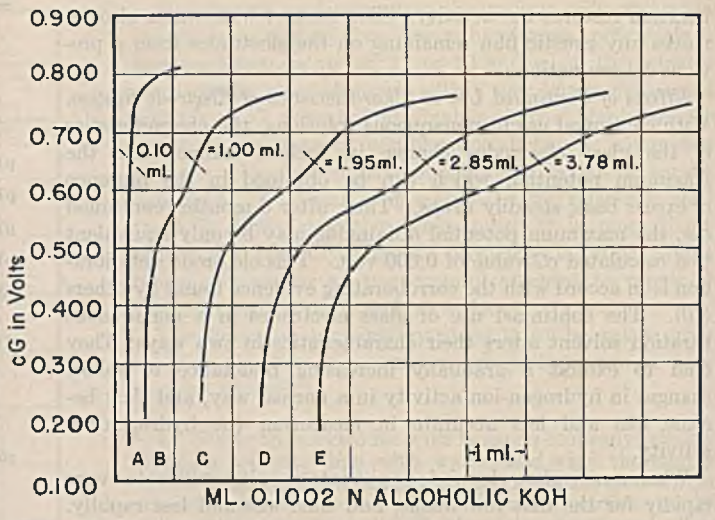

Figure 17. Influence of Sample Size upon Determination of Free Acid

Potentiometric titration of following amounts of oxidized oil with alcoholic potassium hydroxide: *A* 0.00, *B* 2.00, *C* 4.10, *D* 6.11, *E* 8.18 grams
Titration cell. Glass electrode || calomel electrode
Titration solvent. 50 ml. of benzene, 50 ml. of isopropyl alcohol containing 1% water

In order to determine the extent of the errors due to the presence of easily saponifiable material, a standard solution of oxidized oil and castor oil in benzene–isopropyl alcohol titration solvent was employed. This was prepared so that 100 ml. of solution contained 5 grams of oxidized oil and 3 grams of castor oil. Portions (100 ml.) of this solution were titrated to successively higher e.m.f. values with alkali, and were immediately back-titrated with alcoholic hydrochloric acid to see if the curves would retrace themselves—i.e., to determine whether or not saponification had taken place. It was found that the back-titration with acid retraces the base titration curve within the practical limits of experimental error when the titration is stopped at any point below $cG = 0.650$ volt. If the titration is stopped at $cG = 0.709$ volt, a small amount of saponification takes place. Thus, if the end point in the free acid-titration occurs near $cG = 0.650$ volt, it can be safely assumed that no saponification has taken place unless the sample contains esters more readily saponified than castor oil. If the end point occurs above $cG = 0.700$ volt, further evidence that some saponification has not occurred is necessary.

The optimum sample size has been found by experience from the results obtained in a great number of analyses. The main factors governing the choice of sample size were found to be:

1. Amount of precipitated salts formed during titration. This factor applies to free acid and free base determinations only, since the amount of caustic added in the saponification procedure control the amount of salts formed during the titration in the case of combined acid-base determinations. When too much of the flocculent precipitate of salts is formed in the titration vessel, it interferes by occluding some sample. When this happens, the equilibration is slow and the titration curve is abnormal, both conditions producing considerable error.

2. Characteristics of the break. The sharpness of the breaks in the titration curves for oxidized oils depends to a considerable extent upon magnitude of the titration and, for that reason, on the size of sample used. Examples of this dependence are shown for free acid determinations in Figure 17, and for combined acid-base determinations in Figure 18.

While the variation in the characteristics of the samples to which these methods are applicable is so great that general rules for sampling are almost impossible to formulate, the limits given in the methods (*1*, *2*) are known to have given good results with the majority of the samples to which they have been applied.

The potentiometric method has generally been accepted without much comment in those cases where the

Table XII. Comparison of Free Acid Numbers Obtained for Dark Oils by Colorimetric and Potentiometric Methods

Oxidation Test No.	Time of Oxidation	Acid No. Potentiometric method[a]	Acid No. Colorimetric method[b]	Oxidation Test No.	Time of Oxidation	Acid No. Potentiometric method[a]	Acid No. Colorimetric method[b]
	Hours	*Mg. KOH/g.*			*Hours*		
1	0	1.19	Test fails[c]	5	8	1.4	0.6
	8	1.97	0.04		16	1.0	0.7
	16	2.31	0.80		24	2.3	0.7
	24	2.79	0.90		36	3.1	0.7
	36	3.00	1.00	6	8	0.6	0.2
2	8	9.5	6.6		16	1.4	0.4
	16	9.2	4.7		24	1.8	0.6
	24	7.1	4.1		36	2.2	0.9
	36	5.2	3.2	7	8	2.7	0.8
3	8	1.1	0.5		16	4.5	1.6
	16	1.2	0.5		24	4.9	1.5
	24	2.4	0.5		36	5.5	1.5
	36	2.2	0.5	8	8	2.7	0.8
4	8	6.9	4.3		16	4.1	0.5
	16	11.6	6.9		24	4.5	0.9
	24	15.4	7.2		36	5.1	2.0
	36	20.1	8.0				

[a] Designated A.S.T.M. D664-42T.
[b] Designated A.S.T.M. D663-42T.
[c] Test fails owing to inherent color of sample.

Table XIII. Comparison of Combined Acid (Saponification) Numbers Obtained for Dark Oils by Colorimetric and Potentiometric Methods

Sample[a]	A.S.T.M. D94-39T colorimetric	A.S.T.M. D94-41T colorimetric	Total combined acidity, potentiometric	Strong combined acidity, potentiometric
	Saponification Number or Combined Acidity			
	Mg. of KOH per gram			
1	3.5	4.5	3.4	0.2
2	30.6	30.7	30.9	0.7
3	1.2	1.7	1.6	0.6
4	3.6	4.6	4.5	0.3
5	40.2	30.7	28.5	0.5
6	1.0	1.6	0.9	0.3
7	3.4	4.2	4.2	0.2
8	28.8	30.1	28.5	0.3
9	2.5	4.8	3.6	0.5
10	4.9	7.8	7.8	0.6
11	25.2	27.1	27.6	21.3
12	31.4	33.1	35.2	24.7
Degras oil	117.3	121.8	132.0	10.1
Sperm oil	135.6	138.6	139.5	0.6
Sulfurized	167.7	161.6	163.4	26.4

[a] Samples 1 to 12 are oxidized oil samples.

titration curves show definite inflection points or breaks. The potential difference between the electrodes at the inflection point of a given sample varies from one electrode system to another and especially from one laboratory to another. While this variation has no appreciable influence when definite inflections are found, it is significant when the titration curves show no definite inflection points and the results are calculated from the volumes of base or acid required to produce a standard *cG* potential. Therefore, in the absence of definite breaks (less than 0.025-volt change per 0.10 ml. of 0.1 *N* base) the titration is made to the potential found to be equivalent to the standard *cG* = 0.650 volt, or *cG* = 0.236 volt, by a test such as that suggested.

Even under good equilibrium conditions, titrations of some oxidized or used lubricating oils give curves that fail to reach the *cG* value expected for the given amount of base added. This lowering or flattening of the upper part of the titration curve is probably caused by the presence of certain materials having acidic characteristics that buffer the *cG* value in much the same way that certain phenols lower the pH of a dilute aqueous solution of a strong base. Except in the case of oils containing complex metallic salts or dopes, the lowering or flattening of the titration curve is probably not due to the consumption of the base by the acid complexes in a saponification or hydrolysis reaction. Furthermore, the abnormal lowering of the curve probably is not caused by reaction of the base with nonacid constituents of the sludge.

In general, inspection of the titration curves submitted by various laboratories using the potentiometric method indicates that, in many instances, too large increments of standard base were used and a sufficient length of time was not allowed for equilibrium between the increments. Reasonably satisfactory results have been achieved by using a short, constant equilibration period (0.5 to 1 minute) when small, constant increments (0.05 to 0.10 ml. of 0.1 *N*) of base are added, but erratic high results are obtained when large increments of variable size (more than 0.1 ml. of 0.1 *N*) are used with short, constant equilibration periods. If increments of variable size are used, as during a prolonged titration, more satisfactory results are obtained by allowing the electrode system to come to equilibrium after adding each increment. These considerations are especially important in the region of the end point. False breaks are sometimes manifested when a series of large increments is followed by several small increments and insufficient time is allowed for equilibrium.

The methods for free and combined acids and bases given in this paper have been applied to the analysis of over 5000 samples. They have been found extremely valuable in studies of the oxidation of petroleum products, and in the evaluation of a great number of materials. More recently, the methods have been adapted to a semimicro scale; equipment of a special nature has been designed for such small-scale work (*21*).

Isopropyl alcohol, C.P., was chosen as the solvent for the standard acid and base because it is one component of the titration solvent and because caustic solutions made from it are more stable than those made from ethyl alcohol. Special grades of isopropyl alcohol to which odorants may have been added are not recommended for the preparation of these reagents.

In the determination of acidity in complex mixtures, such as lubricating oil or organic distillates, any information which helps to identify the acidic constituents may prove valuable. The potentiometric titration gives such information, and, in addition, furnishes a record of just what took place during the analysis of any sample.

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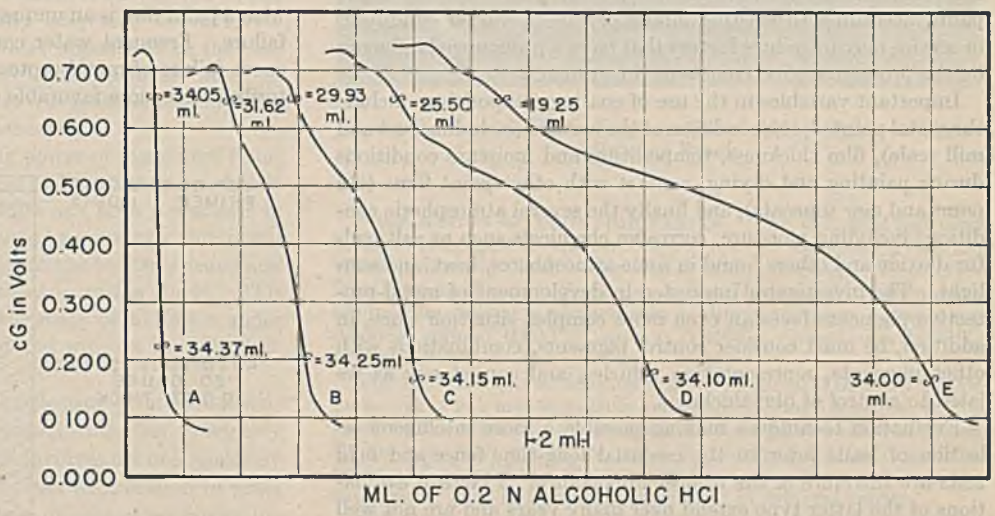

Figure 18. Influence of Sample Size upon Determination of Combined Acids and Bases

Potentiometric titration of basic materials remaining after saponification of following amounts of oxidized oil with potassium hydroxide: *A* 0.00, *B* 1.101, *C* 2.014, *D* 4.029, *E* 8.01 grams
Titration cell. Glass electrode || calomel electrode
Saponification medium. 40 ml. of benzene, 40 ml. of isopropyl alcohol containing approximately 7 milliequivalents of potassium hydroxide

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Laboratory Evaluation of Corrosion-Inhibitive Pigments

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The importance of water condensation in failure of metal-protective paints by corrosion is discussed. Severe-service tests are differentiated from "accelerated" tests. Techniques are described for laboratory evaluation of the corrosion resistance imparted by metal-protective pigments. The preferred technique combines use of thin metal foil panels 0.0005 inch thick, single films or thin films offering minimum physical protection, and exposure under controlled water-condensation conditions.

THIS paper deals with methods for investigating the protective value of corrosion-inhibitive pigments in maintenance paints for metal surfaces, with emphasis on degree of inhibitive action rather than film durability.

Because of the many variables which may be encountered in service, the evaluation of pigmented coating compositions for the protection of structural steel surfaces against atmospheric corrosion represents a most difficult field of testing. For the same reason, apparently conflicting performance data are sometimes obtained in so-called practical tests.

Progress in the development of improved pigments and paints has accordingly been slow and the actual advances represented by new products have been uncertain. Honest differences of opinion may exist as to the relative merit of standard products which have been in extensive use over a number of years. Even after an anticorrosive pigment has been properly formulated into paint, according to existing laboratory tests, varied conditions in service may introduce factors that have a pronounced influence on the protective effectiveness of the system.

Important variables in the use of coating compositions include the metal painted, the condition of the surface (including rust and mill scale), film thickness, temperature and moisture conditions during painting and drying, contact with other paint films (old paint and new topcoats), and finally the several atmospheric conditions including moisture, corrosive chemicals such as salt, sulfur dioxide and others found in some atmospheres, heat, and sunlight. The investigator interested in development of metal-protective pigments faces an even more complex situation since, in addition, he must consider control pigments, combinations with other pigments, representative vehicles, and consistency as related to control of film thickness.

Evaluation techniques making possible a more intelligent selection of leads prior to the essential long-time fence and field tests are therefore of the utmost importance. Practical evaluations of the latter type extend over many years and are not well adapted for exploratory studies. In setting up preliminary laboratory tests, conditions should be selected on the basis of an analysis of the requirements to be met by a metal-protective paint film in accomplishing its objective—namely, prevention of corrosion of the metal. Film requirements include (1) maintenance of continuity, (2) maintenance of adhesion to the metal, and (3) inhibition at the metal-film interface. The pigment influences each of these characteristics but is particularly important in relation to providing protection by passivation and/or exclusion of water and oxygen and/or control of film acidity.

In connection with the development of improved metal-protective pigments, techniques have been devised in this laboratory by which individual protective characteristics of a candidate pigment can be studied under controlled conditions to provide a basis for subsequent exposure work. These are not "accelerated tests", at least in the usual sense of the term, and in particular, they are not accelerated tests in which some one factor has been exaggerated to a degree never met in practice in order to induce some kind of rapid failure. Thus, they are not to be considered in the category of salt-spray and continuous-immersion tests which are frequently used as accelerated tests and accepted as indicating performance under atmospheric conditions but which actually demonstrate performance under special conditions occasionally met in practice. Rather, they are to be considered as "severe-service" tests in which severe conditions which are most likely to cause failure in general service are brought into the laboratory and reproduced as faithfully as possible without intensifying any factor to a degree greater than that actually met in practice. For example, water continuously or frequently in contact with a paint film is an unquestioned factor in promoting corrosion failure. Frequent water condensation in practical service may cause failure of metal-protective paints which stand up satisfactorily under more favorable conditions. Rusting on the bottom

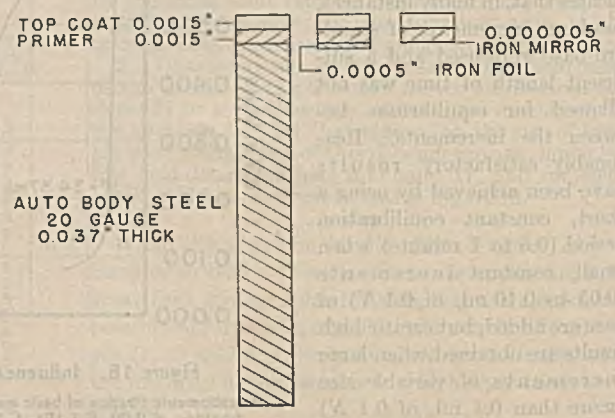

Figure 1. Relative Thickness of Panel Material Used in Testing Effectiveness of Metal-Protective Primers

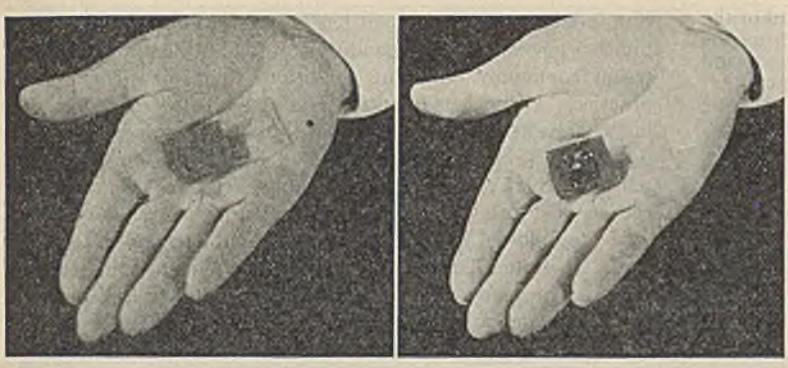

Figure 2. Miniature Iron Foil Panel Painted with Iron Oxide-Linseed Oil
Left. Paint side after exposure. Right. Back of panel. Note underfilm corrosion

surface of steel beams, while sides and top are in good condition, is a common occurrence which can be traced to condensation and hanging water droplets.

In setting up tests to establish corrosion-inhibitive effectiveness, the general rules have been (1) to use only conditions which are actually met in practice, (2) to apply the more severe conditions most likely to induce failure, and (3) to limit the evaluation in so far as practicable to one cause of failure. In the techniques presented, prevention of underfilm corrosion has been emphasized. The ability of the pigment-binder combination to inhibit corrosion directly or to keep corrosion-inducing agents away from the metal is the property under study, with durability and adhesion either minimized or secondary. The importance of the latter two factors is clearly recognized, but they are secondary unless subfilm corrosion is controlled simultaneously.

With regard to the mechanism of corrosion, previous workers have firmly established several points which stand out from the maze of theories and isolated facts in the literature, and furnish guidance in test development. Atmospheric corrosion cannot proceed unless both water and oxygen are present. The process of corrosion may be accelerated by the presence of active acids or certain electrolytes. In service, the atmospheric oxygen factor may be considered constant and the moisture factor the primary atmospheric variable. Atmospheric acidity is undoubtedly involved in some severe failures in service—for example, acidity in the form of sulfur dioxide or trioxide (smoke) and carbon dioxide. Electrolytes may be very important in specific cases and must not be overlooked—for example, sodium chloride from sea water spray or other sources. Film acidity may also be involved. However, in the majority of cases, water appears to be the controlling factor in promoting corrosion under an intact film (excluding durability). Consequently, it was selected for emphasis in developing laboratory severe-service tests.

In studying the corrosion-inhibiting power of pigmented films, it is important to detect the first stages of corrosion and to follow its progress. To this end, a technique has been developed in which the normal metal panel is replaced by extremely thin metal foil representing the immediate surface of the ordinary panel and so thin that perforation occurs as soon as corrosion starts. This "thin foil technique" makes possible the study of inhibition under an intact paint film normally applied and without the introduction of abnormal influences.

In addition, two general techniques reflecting severe conditions occurring in practice have been selected with the previously stated general rules in mind. The first involves use of a relatively thin paint film, a condition which is often encountered in practice and which represents a severe test of protective power because of the greater permeability of the film to water. The second involves moisture condensation, the basis for which has already been discussed.

These three techniques will be described in greater detail, together with adaptations which introduce the further factors of weathering and prerusted steel surfaces.

THIN FOIL TECHNIQUE

The general method comprises the painting of one side of a metal "panel" so thin that a minute amount of corrosion will be apparent from the back or uncoated side of the panel which is protected by sealing it with an inert resin on a transparent glass plate such as a microscope slide. Panels made up from iron foil about 0.0005 inch thick have been extensively used in development studies.

Figure 1 indicates the relative thickness of such thin panels as compared with ordinary 20-gage steel panels and with an ordinary paint film.

Corrosion usually becomes visible from the panel rear before it does through the paint film. This is particularly helpful with dark-colored primers and in cases where topcoats are applied over the primer film. In the case of blistering or questionable areas, it can be seen directly whether or not actual corrosion is involved. Figure 2 shows a painted miniature iron foil panel after an exposure; at left is the paint side and at right the extent of underfilm corrosion as seen from the back of the panel.

The thin foil technique can readily be extended to nonferrous metals such as aluminum and magnesium alloys.

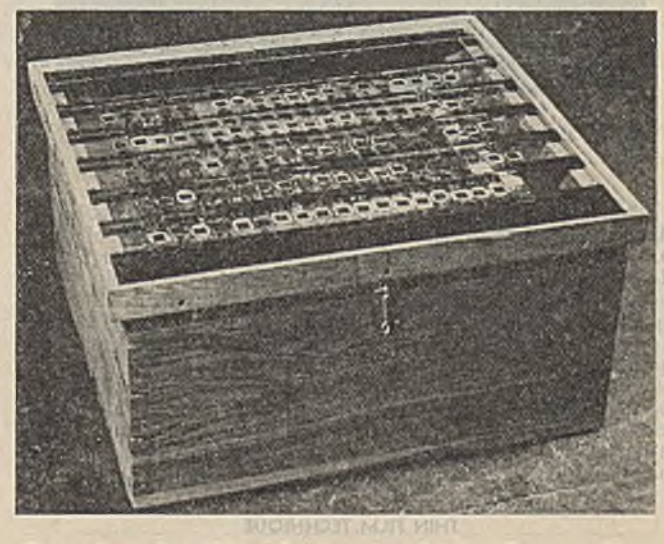

Figure 3. Indoor Water-Condensation Cabinet Open to Show Miniature Panels

Preparation of Thin Foil Panels. The thin iron foil used in this investigation was obtained from the American Platinum Works, Newark, N. J. The iron was described as "Electrolyt-Iron Heraeus-Vacuum-Schmelze A. Ca., Hanau, a.M., Germany", having the following elements in addition to iron: manganese, 0.030%; silicon, 0.030%; carbon, 0.010%; phosphorus 0.008%; sulfur, 0.016%.

The foil used has a thickness of the order of 0.0003 to 0.0005 inch. It is cut into miniature panels (0.625-inch squares) with a paper cutter after being placed within the fold of a sheet of paper. Before use, each miniature panel is examined for freedom from holes and blemishes. To protect from premature rusting, the small squares of foil are kept immersed in mineral spirits.

The technique used in mounting the miniature foil panels is as follows:

Clean microscope slides (3 × 1 inch) are laid on an electric hot plate and heated until the glass-to-metal adhesive, an inert ether resin of the type disclosed in U. S. Patent 2,060,715, melts and adheres when rubbed on the hot glass surface. Sufficient adhe-

sive is transferred in this manner to cover the central third of the glass slide with a thin film. The slide is then removed from the hot plate with a forceps and one of the 0.625-inch squares of foil is transferred to the central fluid resin area. Intimate contact of resin to metal is secured before the resin solidifies by pressing the metal foil with the end of a bar very slightly smaller in cross section than the piece of foil. If there is a tendency for the edge of the foil to turn up, a small spatula with turned up point is used to seal these edges by pressure. The mounted foil is ready for painting when cool. If painting is delayed, the mounted foil panel is kept in a desiccator to protect against atmospheric corrosion. The sealing resin must be inert to avoid the possibility of corrosion from this source, and it must retain its bond to glass in the presence of water. Turned up edges of the foil should be avoided, since they will later cut the paint film and end the test prematurely.

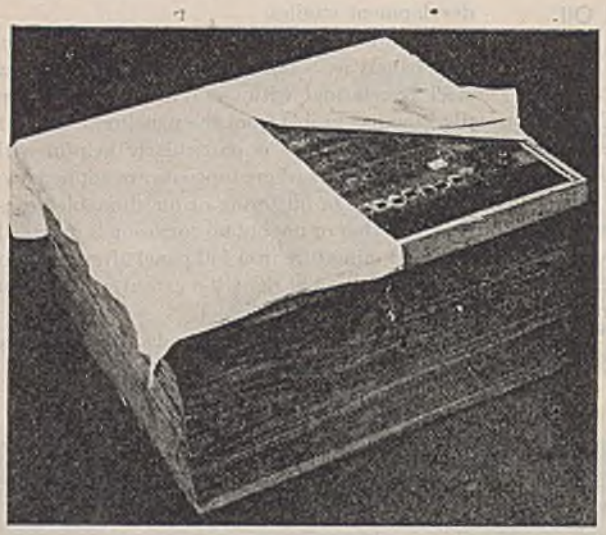

Figure 4. Indoor Water-Condensation Cabinet Covered by Glass Plate and Wet Towels

The miniature panel is painted with a flat 0.5-inch brush. Attention is given to securing a "normal" film thickness of about 0.0015 inch except where a test of the effectiveness of thin films is desired (see below). This is done by using a relatively "dry" brush and first painting out each system on a specimen area corresponding to the miniature foil panel. The amount of paint to be applied to the foil area is the amount necessary to give the required increase in weight on the test specimen area. When the effect of a topcoat is to be tested, the latter is applied over the primer in a similar manner after a suitable drying period. Almost insignificant amounts of paint materials are required, and it is therefore imperative that the brush used be clean of other paint and dry of solvents.

THIN FILM TECHNIQUE

Primed metal without topcoat is frequently exposed to atmospheric influences for long periods. Since this represents a severe test of inhibitive effectiveness, a single primer coat has been used in much of the routine testing of pigments in this laboratory.

Where a particularly severe, yet practical, test of inhibition is desired, the normal thickness of the primer film, 1.5 to 2 mils, is reduced by about 50%. This is legitimate, since practical painting practices frequently result in thin areas of film. Improper thinning of normally effective paints in service has been known to produce early failure for this reason. The film thickness factor is especially important if the primer is expected to be the sole protecting film over a long period of time, as is the case with shop-primed maintenance steel. For these reasons, it is frequently desirable to determine the performance of metal-protective pigments in a thinner paint film than would be recommended.

WATER-CONDENSATION TECHNIQUE

Because of the fundamental dependence of extent of corrosion on degree of moisture condensation, controlled water condensation in laboratory equipment has been used for evaluation of inhibitive power, selecting conditions which, although severe, represent commonly occurring conditions that cause corrosion in practice. Heavy condensation is a general phenomenon, existing wherever the temperature of the metal object drops below the dew point, and may be encountered wherever atmospheric humidity is relatively high, as in the vicinity of a stream or near the seacoast or in a damp basement or tunnel, or wherever warm days are followed by cool nights with rapid decrease in temperature. It occurs daily in the tropics and frequently in other regions. The degree of corrosion is also governed in large measure by the frequency of long damp periods. Choice of a wet/dry condensation cycle can be made in specific cases to adjust the severity of the exposure to correspond to that of any condition in any climate.

Two types of condensation tests have been used, an indoor test involving alternate periods of condensation and drying without weathering, and an outdoor test comprising alternate periods of condensation and exposure outdoors 45° south. Each contributes useful information and the two preferably should be run in parallel. Both sets of conditions are met in practice.

Two water-condensation cycles have been used in laboratory service tests. The "daily cycle" involves a wet period of water condensation at night and a dry period during the daytime, corresponding to the diurnal variation that often occurs. The "weekly cycle" of 4 days wet and 3 days dry is used to simulate the effect of frequently occurring damp periods. For the film-metal systems studied, corrosion was definitely more rapid for the weekly cycle than for the daily cycle, even though the wet fraction of the total cycle is about the same. Corrosion in the daily cycle is much more severe than in the much shorter cycles of some "accelerated tests" where the wet to dry change takes place considerably more frequently (such as at 15- to 60-minute intervals), there being less chance for either a dry or wet equilibrium condition to be developed in the film. The exact significance of the dry portion of the cycle has not been established. However, it affords an opportunity for migration of water-soluble components of the film which theoretically may occur.

The results of indoor water condensation tests should be interpreted only in the light of the purpose for which the test was designed, to show the behavior of film systems when used under conditions involving relatively prolonged water condensation and no exposure to outdoor weathering. The indoor tests do not show the specific effects of sunlight on the ultimate durability of the system but they do emphasize the inhibitive value of the film.

Outdoor exposure at 45° south can be included intermittently

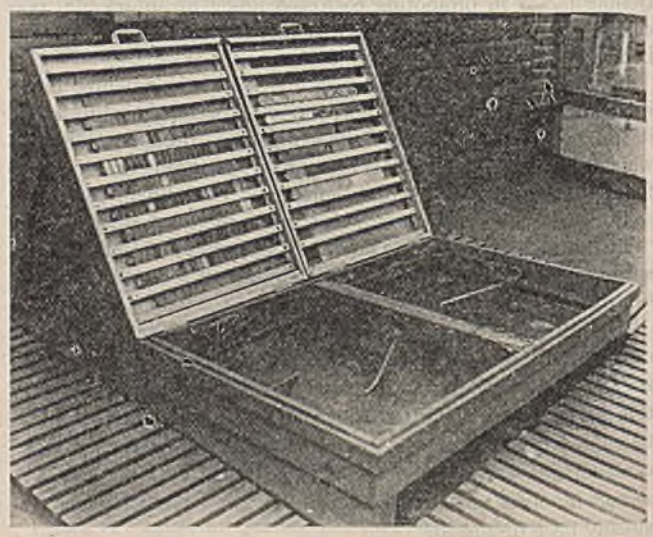

Figure 5. Outdoor Water-Condensation Cabinet

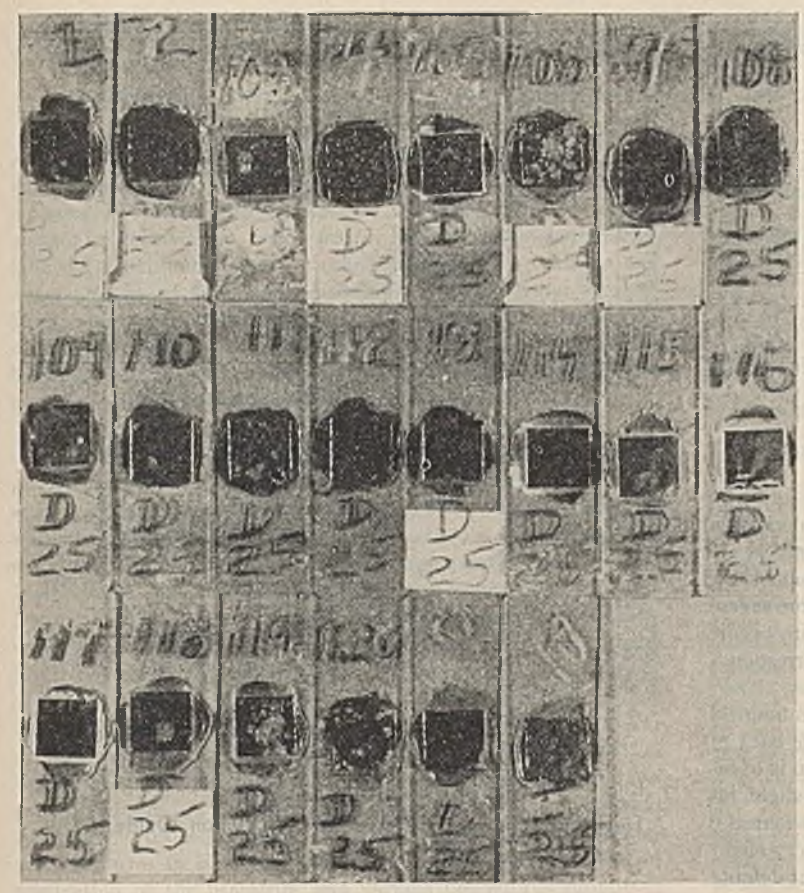

Figure 6. Typical Underfilm Corrosion

Rear view of painted miniature iron foil panels after exposure
Corrosion of simple single-pigment–linseed-oil primer systems after exposure in indoor water-condensation cabinet under selected conditions

with the cycle for the indoor box, where this type of information is desired.

Water-Condensation Cabinet, Indoors. The panels are exposed painted side downward between bars suspended over the top of wooden boxes about 24 × 24 × 12 inches deep (see Figures 3 and 4). The top edge of the box is recessed to receive a snugly fitting plate-glass cover, which is supported about 0.125 inch over the panels. The box is waterproofed by waxing inside. A wide tray containing water covers the bottom of the box and may be reached through a door in the side. If the number of exposure panels is insufficient to cover the top area of the box completely, "dummy" panels are used to fill up the space, so that the system is a closed one even before the glass plate is put in place. A wet towel is placed over the glass plate and kept wet. Continuous evaporation from the towel maintains the temperature of the panels in the box at or below the dew point. In this closed water-saturated system, fine water droplets condense and remain on the painted side of the panels. The box is deep to facilitate regulation of the pH of the condensed water if it is desired to investigate the effect of acid dews (such as with sulfur dioxide).

A somewhat simpler although less flexible arrangement is one in which the deep box is replaced by a relatively shallow tray, and the panels are directly sealed (paint side exposed) to the bottom of the large glass cover with a beeswax-rosin mixture. The cover may be kept cooled by a thin layer of water retained thereon by a shallow wax dam around its edges or by the above towel arrangement.

Water-Condensation Cabinet, Outdoors. The general arrangement for outdoor exposure is essentially the same as that of the indoor box, with the added feature that the cover is hinged and the panels are fastened thereto in a manner permitting them to be exposed at 45° facing south by swinging the cover back on its hinge 135° from the normal face-down position (see Figure 5). The top of the box is plate glass sealed in the wood frame so as to provide a tray. In the summer months, condensation is promoted on the panels by the cooling induced by evaporation from a 0.25-inch layer of water maintained in this tray when the box is closed. During other seasons when the temperature is low outdoors, no cooling water is needed but several low-wattage immersion heating coils are required in the interior water tray to ensure the necessary temperature differential for condensation. The water is maintained about 10° F. above the air temperature when it is necessary to use the heaters.

Exposure Cycle. For the indoor condensation tests, two wet/dry cycles have been used. The daily cycle corresponding to that of the outdoor box is not so effective in producing corrosion as is the weekly cycle consisting of 4 days of continuous condensation and 3 days dry. This latter period has been used to the greatest extent, inasmuch as it is considered to simulate the effect of frequently recurring condensation during humid periods or in damp locations. The daily cycle corresponds more nearly to heavy condensation conditions in the absence of direct sunlight.

The outdoor arrangement is best adapted to a daily cycle with water condensation at night and exposure at 45° south during the day. For convenience, a wet/dry cycle of 15/9 hours has been used in the work to date. A weekly cycle comparable to that used in indoor tests appears to have promise but has not been explored thoroughly.

PERFORMANCE

Reproducibility of Results. As in all corrosion evaluation, it is advisable to make at least duplicate and preferably triplicate panels. General experience has been that results with the miniature panels are readily reproducible. Performance has been much more consistent than for ordinary large panels on outdoor rack tests.

Time Required for Tests. The time required for significant results depends on the efficacy of the protective systems and on

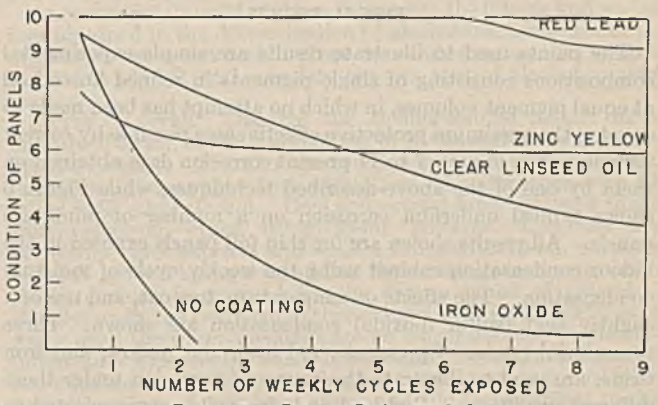

Figure 7. Primer Only, 25° C.

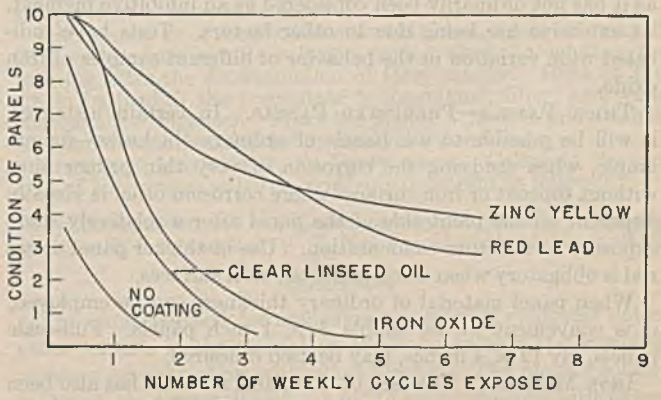

Figure 8. Primer Only, 25° C., SO_2 Condensate (pH 5.0)

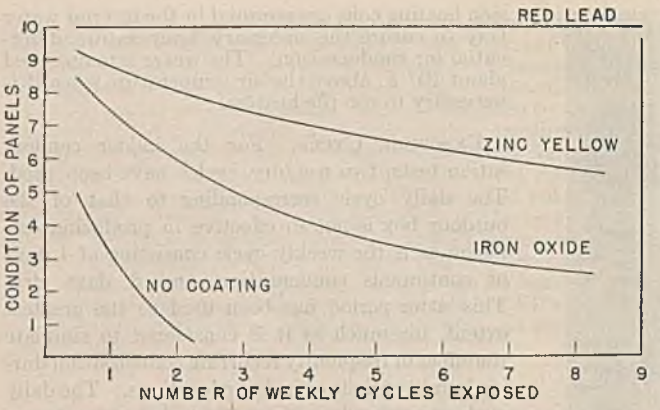

Figure 9. Primer and Topcoat, 25° C.

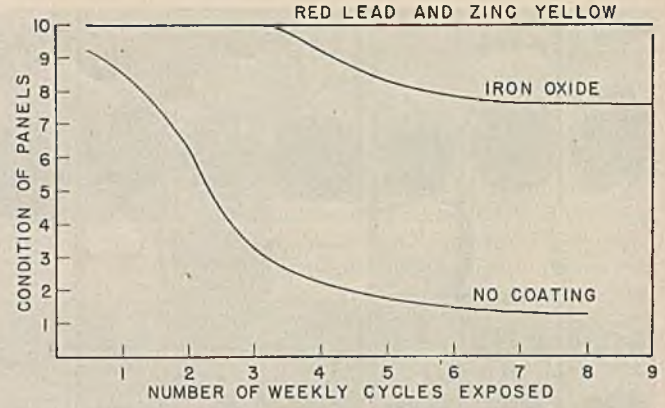

Figure 10. Primer and Topcoat, 5° C.

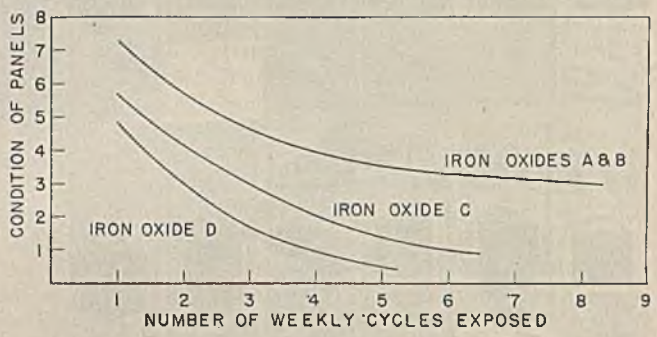

Figure 11. Primers, Different Grades of Iron Oxide, 25° C.

the cycle chosen. In the case of an outdoor water-condensation box with a daily cycle, differences among the poorer systems are often apparent within a month or two, while some systems show failure only after 10 months or so. In the case of the more severe condensation test using the weekly cycle, similar failure occurs indoors within shorter time intervals—i.e., within the corresponding number of weeks.

Method of Grading. The panels are graded on a numerical basis after visual examination of both the front and the back of the panel. Inasmuch as the early incidence of corrosion is of interest, a grading code has been used that emphasizes slight initial changes. A grading of 10 represents no rusting, whereas 0 represents complete failure. A grading of 9 denotes very slight (even questionable) corrosion, while 8 indicates slight but definite corrosion, and 7 corresponds to failure of about 10% of the metal surface area. Gradings from 7 to 0 are in proportion to the surface area remaining unattacked—i.e., from 90 to 0%.

TYPICAL RESULTS

The paints used to illustrate results are simple experimental compositions consisting of single pigments in refined linseed oil at equal pigment volumes, in which no attempt has been made to develop the maximum protective effectiveness possible by correct formulation. Figures 7 to 11 present corrosion data obtained on them by one of the above-described techniques, while Figure 6 shows typical underfilm corrosion on a number of miniature panels. All results shown are for thin foil panels exposed in the indoor condensation cabinet using the weekly cycle of moisture condensation. The effects of temperature, topcoat, and use of a slightly acid (sulfur dioxide) condensation are shown. Three commercial grades of pigments, red lead, zinc yellow, and iron oxide, are used to illustrate the course of corrosion under these different conditions. Red lead and zinc yellow were selected as typical inhibitive pigments. Iron oxide was selected inasmuch as it has not ordinarily been considered as an inhibitive pigment, its extensive use being due to other factors. Tests have indicated wide variation in the behavior of different samples of iron oxide.

Thick Panels—Prerusted Panels. In certain instances, it will be possible to use panels of ordinary thickness—for example, when studying the corrosion of very thin primer films without topcoat or iron surfaces where corrosion often is visually apparent on the paint side of the panel after a relatively short exposure to moisture condensation. Use of thicker panel material is obligatory when using prerusted steel surfaces.

When panel material of ordinary thickness can be employed, it is convenient to use simple 3 × 1 inch panels. Full-scale panels, say 12 × 4 inches, may be used if desired.

Iron Mirrors. The idea of thin panel material has also been carried to an extreme by the use of translucent iron mirrors. This system is so sensitive that it has not to date been useful from the standpoint of the objective of this paper—namely, evaluation of practical metal-protective pigments. However, the technique itself is briefly described because of its possible utility as a tool in studying theoretical aspects of the effect of pigments in preventing corrosion.

Translucent iron mirrors were prepared by evaporating relatively pure iron on a heated tungsten filament under high vacuum, the mirror being formed by condensation of the iron vapor on a 3 × 1 inch microslide in the evacuated system. Mirrors having a thickness of the order of 0.000004 inch (1000 Å.) were selected, selection being on the basis of visual density of the mirror film. The thickness has been checked by an interferometric method and by a colorimetric analysis for iron.

The iron mirror film is relatively stable to corrosion in the ordinary laboratory atmosphere. Under high humidity conditions, however, the film fails. Extremely thin mirrors are unsuitable because they fail by microcracking and microcurling at high humidity. Thicker, but still translucent, mirrors show the typical micro "pitting" type of corrosion when exposed for a week or two in an atmosphere of high humidity. An area of bright yellowish-brown rust appears at or near the center of the pit and appears to grow at the expense of the retreating iron mirror.

ACKNOWLEDGMENT

Acknowledgment is made to the Pigments Department of E. I. du Pont de Nemours and Company, Inc., which supported this work and provided for the photographic reproduction of the outdoor water-condensation cabinet at the Newark, N. J., laboratory. Appreciation is expressed to members of staffs of the Pigments Department and of the Chemical Department for assistance in experimental work.

Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa. Contribution 196, Chemical Department, E. I. du Pont de Nemours and Company, Inc.

Analysis of Soap–Synthetic Detergent Mixtures in Bar Form

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A procedure for the analysis of commercial soap–synthetic detergent mixtures is proposed which has given sufficiently accurate and reproducible results. The sample is extracted with 95% ethyl alcohol to remove the major portion of the active ingredients, followed by solution of the alcohol-insoluble salts in water and reprecipitation of them by the addition of excess ethyl alcohol. Soap, fatty matter, and alcohol-soluble chlorides are determined directly, synthetic detergent being determined as the difference between total alcohol-soluble matter and the sum of soap, fatty matter, and alcohol-soluble chlorides.

A BAR form of soap–synthetic detergent mixture has recently come into wide use by the Navy for general cleaning in sea water. Several publications have described the use of soap–synthetic detergent mixtures as replacements for coconut oil soaps which are no longer available in large quantities (*3*, *11*, *12*). Methods for analyzing these mixtures are being used by manufacturers for their own products, but as yet, except for a method contained in a government specification for bar form of salt-water detergent (*2*), no general procedure for the analysis of such mixtures has appeared in the literature. Inasmuch as the Navy Department is a large consumer of soap–synthetic detergent mixtures in bar form which must conform to specification requirements, it is important that an accurate method of analysis be available. This paper presents a sufficiently accurate and reproducible procedure for the analysis of soap–synthetic detergent mixtures in bar form, which was developed after an investigation of the literature and various procedures submitted by several soap and synthetic detergent manufacturers.

Methods for the direct determination of synthetic detergents have been reported (*1*, *4–7*, *10*), but none has been applied to the analysis of soap–synthetic detergent mixtures. Moreover, these methods are applicable only to those detergents whose exact structure is known, and cannot be used for commercial soap–synthetic detergent mixtures in which the synthetic portion is not identified and may consist of a mixture of indefinite composition.

Soap–synthetic detergent mixtures of the type useful for salt-water cleaning consist of an active portion (soap and synthetic detergent) and an inactive portion (inorganic salts, moisture, and fatty matter). The term "fatty matter", as used in this paper, refers to all constituents preferentially soluble in petroleum ether; this will normally include hydrocarbons, fats, and free fatty acids. The term "active ingredient", as used in this paper, is applied to the alcohol-soluble portion corrected for determined impurities. The present method is based on the separation of active ingredients from inorganic salts by means of ethyl alcohol, and the subsequent determination of soap, fatty matter, and sodium chloride in the alcohol-soluble portion. Synthetic detergent is calculated as the difference between total alcohol-soluble matter and the sum of soap, fatty matter, and alchohol-soluble sodium chloride.

PROCEDURE

ANHYDROUS, SALT-FREE SODA SOAP. Weigh to the nearest milligram a 2-gram sample of the soap–synthetic detergent bar in a tared 300-ml. Erlenmeyer flask. Add 50 ml. of water and 50 ml. of 95% ethyl alcohol. (Formula 2B or 30 alcohol may be used if 95% ethyl alcohol is not available.) Warm on the steam bath until no further solution takes place. Cool, add 5 drops of methyl orange indicator, and titrate with 0.5 *N* sulfuric acid to a pink color. Add 5 to 6 ml. in excess. Transfer the contents of the flask to a 500-ml. separatory funnel, washing out the flask with 50 ml. of water, then with 50 ml. of ethyl alcohol. Add the washings to the separatory funnel. Extract the fatty acids and fatty matter 4 times with petroleum ether, using 40-ml. portions. Combine the petroleum ether extracts and wash with small portions of distilled water until the water washings are no longer acid to methyl orange.

Transfer the petroleum ether extracts to the original 300-ml. tared flask, filtering if necessary, and wash the separatory funnel with 2 small portions of petroleum ether, adding the washings to the flask. Evaporate the petroleum ether on the steam bath, then dry in an oven at 100° to 105° C. to constant weight. Cool and weigh as fatty acids plus fatty matter.

Dissolve the fatty acids and fatty matter in 50 ml. of neutral ethyl alcohol with warming; add phenolphthalein indicator and titrate with standard alcoholic 0.1 *N* sodium hydroxide.

Calculate the per cent of soap plus fatty matter as follows:

$$\text{Per cent of soap + fatty matter} = \frac{(\text{ml. of NaOH} \times \text{normality factor} \times 0.022) + (\text{weight of fatty acids + fatty matter})}{\text{weight of sample}} \times 100$$

Calculate per cent of soap by subtracting from this value the per cent of fatty matter determined later.

ALCOHOL-INSOLUBLE MATTER. Weigh to the nearest milligram a 2-gram sample in a 250-ml. beaker, add 100 ml. of 95% ethyl alcohol, cover the beaker, and heat on the steam bath with frequent stirring and maceration of the sample until it is completely disintegrated. Let settle and filter through a tared Gooch crucible with suction into a tared 300-ml. Erlenmeyer flask, retaining as much of the residue as possible in the beaker. Repeat this extraction 3 times with 25-ml. portions of hot 95% ethyl alcohol, each time retaining as much of the residue as possible in the beaker. Finally, evaporate any remaining alcohol and dissolve the residue in the smallest possible quantity of hot distilled water (5 ml. should be sufficient). Reprecipitate the alcohol-insoluble matter by slowly adding with vigorous stirring 50 ml. of 95% ethyl alcohol. Heat the solution to boiling on the steam bath, filter, and transfer the precipitate to the Gooch crucible, washing several times with 95% ethyl alcohol. Dry the crucible at 100° to 105° C. to constant weight and calculate the per cent of alcohol-insoluble matter. Reserve the combined filtrate and washings.

ALCOHOL-SOLUBLE MATTER. Evaporate the filtrate and washings obtained in the determination of alcohol-insoluble matter to dryness on the steam bath. Heat the residue to constant weight at 100° to 105° C. and calculate the per cent of alcohol-soluble matter.

FATTY MATTER. Dissolve the alcohol-soluble matter in a mixture of 50 ml. of water and 50 ml. of 95% ethyl alcohol, warming if necessary. Transfer the solution to a 500-ml. separatory funnel, washing out the flask with 50 ml. of water, then with 50 ml. of 95% ethyl alcohol. Cool and extract fatty matter 4 times with petroleum ether, using 25-ml. portions. Combine the petroleum ether extracts and wash 4 times with 10-ml. portions of 0.2 *N* sodium hydroxide, adding the washings to the alcoholic solution which is reserved for the determination of chlorides. Finally, wash the petroleum ether extract with small portions of water until the water washings are no longer alkaline to phenolphthalein. Transfer the washed petroleum ether extract to a tared 300-ml. Erlenmeyer flask, washing out the separatory funnel with 2 small portions of petroluem ether, and add the washings to the flask. Evaporate the petroleum ether on the steam bath and dry the residue at 100° to 105° C. to constant weight. Calculate the per cent of fatty matter.

CHLORIDES IN ALCOHOL-SOLUBLE MATTER. Add 15 ml. of 20% magnesium nitrate solution to the alcoholic solution remaining after the determination of fatty matter. Heat on the steam bath until the precipitate is coagulated, filter, and wash thoroughly with water. Make the filtrate acid with dilute nitric acid and determine chlorides by the Volhard method.

SYNTHETIC DETERGENT, BY DIFFERENCE. Calculate the per cent of anhydrous, salt-free, synthetic detergent as follows:

$$\%\ \text{synthetic detergent} = (\%\ \text{alcohol-soluble matter}) - (\%\ \text{soda soap} + \%\ \text{fatty matter} + \%\ \text{NaCl in alcohol-soluble matter})$$

DISCUSSION

The usual method for analyzing commercial synthetic detergents consists in the separation of alcohol-soluble and insoluble portions by extraction with ethyl alcohol. The alcohol-soluble portion is then generally considered to be "active synthetic deter-

Table I. Adsorption of Synthetic Detergents

(Values represent average of 4 individual determinations, expressed as per cent of total sample)

Sample	Loss in Weight on Ignition of Alcohol-Insoluble Residue		Alcohol-Soluble Matter Recovered from Precipitate of Alcohol-Insoluble Salts		Synthetic Detergent	
	Method I[a]	Method II[b]	Method I	Method II	Method I	Method II
1	4.1	0.9[c]	8.3	0.0	37.1	46.3
2	2.2	0.1	5.0	0.0	34.9	40.9
3	1.5	0.2	4.0	0.0	30.5	34.7
4	4.9	0.3	5.7	0.0	47.2	53.8
5	1.5	0.1	1.4	0.0	19.9	22.0
6	2.8	0.4	3.4	0.0	25.6	29.7
7	1.8	0.3	3.6	0.0	22.8	26.9
8	1.2	0.2	3.2	0.0	17.1	21.1

[a] Method I, no reprecipitation of alcohol-insoluble matter.
[b] Method II, reprecipitation of alcohol-insoluble matter.
[c] High result probably represents loss of water of hydration of borax which is present in this sample.

Table II. Analyses of Known Soap–Synthetic Detergent Mixtures

Determination	Mixture 1		Mixture 2		Mixture 3		Mixture 4		Mixture 5	
	Present	Found	Present	Found	Present	Found	Present	Found	Present	Found
	%	%	%	%	%	%	%	%	%	%
Alcohol-soluble matter	77.7	77.8	67.8	67.9	74.0	74.0	81.1	81.1	74.8	74.5
Alcohol-insoluble matter	22.3	22.4	32.2	32.0	26.0	26.0	18.9	18.8	25.2	25.2
Soap + fatty matter	44.5	44.3	43.2	43.1	41.3	41.2	48.6	48.9	46.2	46.2
Fatty matter	1.3	1.1	4.4	4.4	2.0	2.0	1.2	1.2	0.8	0.8
Soap	43.2	43.2	38.8	38.7	39.3	39.2	47.4	47.7	45.4	45.4
Chlorides	1.2	1.3	4.7	4.7	2.6	2.6	1.1	1.1	0.8	0.8
Synthetic detergent	32.0	32.2	19.9	20.1	30.1	30.2	31.4	31.1	27.8	27.5
Sum of alcohol-insoluble matter, chlorides, soap, synthetic detergent, and fatty matter	100.0	100.2	100.0	99.9	100.0	100.0	100.0	99.9	100.0	99.7
Type of soap used			Toilet Soap					Oleic acid soap		
Synthetic detergent used		A		B		C		D		E

gent". Low results were always obtained by this procedure in this laboratory. In the analysis of soap–synthetic detergent mixtures by the above alcohol-extraction method, low results for synthetic detergent were also obtained. These low results are caused by the fact that some synthetic detergent is adsorbed by the alcohol-insoluble salts: (1) When the residue of alcohol-insoluble matter was dried in an oven at 105° C. and then ignited at 500° C., the loss in weight in some instances amounted to almost 5% of the total sample. (2) The residue of alcohol-insoluble matter foamed in water, indicating the presence of some active material, which might be soap or synthetic detergent. (3) The residue of alcohol-insoluble matter formed a very turbid solution upon the addition of Pedersen's reagent, which does not react with soaps or the salts present (*9*).

Investigation showed that the adsorption of synthetic detergent by the alcohol-insoluble residue can be very greatly reduced and the separation made more complete by a procedure which involves initial extraction of the sample with 95% ethyl alcohol to remove the major portion of the alcohol-soluble matter, followed by solution of the residue in the smallest possible quantity of water and precipitation of the inorganic salts by the addition of ethyl alcohol.

To determine directly the amount of adsorption, samples were extracted with ethyl alcohol, and the residue of alcohol-insoluble matter was filtered on a Gooch crucible, dissolved in the minimum amount of hot water, and reprecipitated by the addition of excess ethyl alcohol. The precipitate was filtered off and the filtrate evaporated to dryness and weighed. This weight represented the amount of synthetic detergent which could be recovered from the thoroughly extracted residue by solution and reprecipitation.

The results in Table I show that the adsorption of synthetic detergent by the alcohol-insoluble residue, as indicated by (1) loss in weight upon ignition of the alcohol-insoluble residue and (2) recovery of synthetic detergent from the alcohol-insoluble residue, can be markedly reduced when the reprecipitation procedure is employed. Values for the synthetic detergent portion of eight samples by the nonprecipitation and precipitation methods are also given in Table I.

Samples 1, 2, 3, and 4 were four commercially available synthetic detergents. Sample 1 was the sodium salt of a sulfonated straight-chain hydrocarbon; samples 2 and 4 were sodium salts of alkyl aryl sulfonates; sample 3 was the sodium salt of a sulfonated glyceryl ester of a straight-chain fatty acid. Samples 5, 6, 7, and 8 were mixtures in bar form of soap and the above synthetic detergents.

In addition to giving incomplete separation of alcohol-soluble matter from alcohol-insoluble salts, most of the methods investigated gave incorrect values in the determination of soap, chlorides, and fatty matter. As the synthetic detergent is determined by difference, the values reported for it may be correspondingly inaccurate. Experience with the submitted methods showed that soap values tended to be low and fatty matter values high, while the difficulty in determining the end point in the chloride determination led to either high or low values.

It is believed that the low values obtained for soap are due to the incomplete decomposition of the soap and consequent incomplete extraction of the fatty acids when mineral acid is added only to a methyl orange end point. Judging from the results obtained, the small excess of acid added in the proposed method is sufficient to decompose the soap completely, but insufficient to decompose the synthetic detergents used.

The high values obtained for fatty matter are believed to be due to solution of acid soaps in the ether used for extraction. Such acid soaps cannot be removed by washing with water alone (*8*). Washing the petroleum ether solution of the fatty matter with dilute alkali seems to overcome this difficulty.

APPLICATION OF METHOD TO KNOWN MIXTURES

Inasmuch as no referee method exists for the analysis of commercial soap–synthetic detergent mixtures in bar form, the present method was tested by analyzing mixtures of known composition, containing soap, synthetic detergent, sodium sulfate, fatty matter, and sodium chloride.

The mixtures were prepared by dissolving the constituents in 50% alcohol, diluting to a definite volume, and taking aliquots for the analyses.

The fatty matter used in the mixtures was obtained by extraction of the synthetic detergent in the commercially available form with petroleum ether in a Soxhlet extractor. The filtered petroleum ether solution was then washed thoroughly with 50% alcohol, evaporated, and dried to constant weight at 105° C. and this extract was used to furnish the fatty matter.

The material left in the Soxhlet after extraction with petroleum ether was extracted with absolute alcohol to remove alcohol–soluble synthetic detergent. The alcoholic solution was then evaporated and dried to constant weight, and after being corrected for sodium chloride present was used in the preparation of known mixtures.

The soap used in the mixtures was obtained by first extracting solutions of two commercial soaps with petroleum ether to remove unsaponified and unsaponifiable matter. The residue obtained on drying was dissolved so far as possible in alcohol and the filtered alcoholic solution evaporated to dryness and to constant weight. This residue, corrected for glycerol and sodium chloride present, was used in the mixtures.

Table II gives values obtained by the proposed method on 5 known mixtures. Synthetic detergent A is the sodium salt of a sulfonated glyceryl ester of a straight-chain fatty acid; B and C

Table III. Analysis of Known Soap–Synthetic Detergent Mixture Prepared in Bar Form

Type of soap, toilet soap. Synthetic detergent, sodium salt of a sulfonated amide of a straight-chain fatty acid)

Determination	Present	Found
	%	%
Alcohol-soluble matter	72.1	72.0
Alcohol-insoluble matter	27.9	27.7
Synthetic detergent	23.4	23.3
Soap	46.6	46.5
Chlorides	2.1	2.2
Fatty matter	0.0	0.0

are sodium salts of alkyl aryl sulfonates; D is the sodium salt of a sulfonated amide of a straight-chain fatty acid; E is the sodium salt of a sulfonated straight-chain hydrocarbon.

In order to guard against the possibility that results obtained by the proposed method on a mixture in bar form, as opposed to mixtures reported in Table II, might be incorrect, an additional sample of known composition made up in bar form was analyzed. The results as given in Table III are of satisfactory accuracy. The figures given are on the anhydrous basis.

ACKNOWLEDGMENT

The authors are indebted to R. C. Hughes and C. W. Schroeder (present address, Continental Foods Corp., Hoboken, N. J.) of this laboratory for their many helpful suggestions, and also to the following for suggested methods: Jay C. Harris, Monsanto Chemical Company; Armour and Company; American Cyanamid and Chemical Corporation; General Dyestuff Corporation; L. F. Hoyt, National Aniline Division, Allied Chemical and Dye Corporation; and Colgate-Palmolive-Peet Company. They are indebted to Lever Brothers Company for suggesting the use of 50% alcohol solution for dissolving the sample, and to J. H. Shipp and Harold Jones of E. I. du Pont de Nemours and Company for a suggested method of analysis and for supplying the sample of Pedersen's reagent.

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The views in this article are those of the authors and should not be construed as the official views of the Navy Department.

A Carr-Price Reagent Dispenser

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THE saturated chloroform solution of antimony trichloride, used in the chemical determination of vitamin A, must be kept under anhydrous conditions at all times, and provision must be made for rapid dispensing of accurately measured volumes.

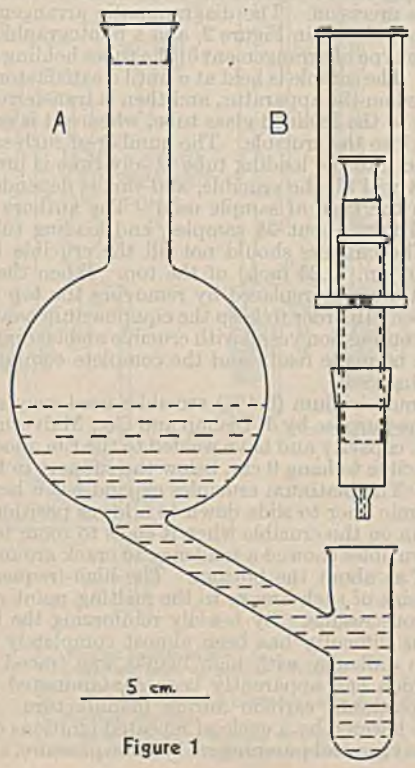

Figure 1

An ordinary pipet is unpleasant to use with this solution and is slow in delivery. The apparatus described serves to solve the problem where a considerable number of determinations are to be made.

A constant-level reservoir for the reagent (Figure 1, *A*) consists of a 300-ml. flask (or other convenient size) with an angular bottom offset leading to a side-arm reservoir wide enough for insertion of a 10-ml. Luer hypodermic syringe. To fill the reservoirs the small one is stoppered and the solution is added to the large one, which is then securely stoppered. The liquid level in the small reservoir remains constant when liquid is withdrawn therefrom.

The solution is removed in measured volume by a hypodermic syringe (Figure 1, *B*) with needle removed, fitted with a brass collar which can be clamped on the syringe barrel. A wrapping of surgical tape on the barrel forms a firm cushion for the collar. Two vertical rods are soldered to the collar and the limiting distance to which the syringe plunger may be withdrawn is governed by a swiveling top bar which may be turned aside when the plunger is to be removed. A stopper around the barrel assures its suitable depth of immersion in the small reservoir and excludes contact between solution and atmospheric moisture. A pipet of similar principle but not suited to the present purpose was described by Krogh (*1*). A paper which appeared after submission of this note includes another design of apparatus for the same purpose (*2*).

For accurate measurement the plunger must be inserted in definite position of orientation with respect to the barrel. This is maintained by suitable markings on the syringe parts.

Tests, using water, gave four successive delivery weights of 9.02, 9.05, 9.03, and 9.04 grams. No tendency for the syringe orifice to drip during transfer was encountered. The syringe should not be left overnight without washing, as there is danger of freezing due to deposition of antimony trichloride. Rubber stoppers should be changed periodically because of attack by the reagent. The solution should be kept in the reservoir only during its actual use to avoid possible contamination from the rubber stoppers.

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Determination of Carbon by the Low-Pressure Combustion Method

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The apparatus for the low-pressure combustion method of determining carbon in iron and steel has been redesigned to increase the speed of manipulation. Several thousand determinations showed results in good agreement with Wooten and Guldner's form of the apparatus. A detailed description of the equipment and its manipulation is given, together with an account of experimental studies on the method. Results are also shown for the carbon content of copper.

THROUGH the kindness of Wooten and his associates, the method of carbon analysis described in his recent paper (*13*) was shown to the authors in the spring of 1938. The desirability of securing accurate data on the carbon content of silicon steels induced them to investigate the possibilities of this method for types of steel which consist largely of iron with silicon ranging from 3 to 6%. Since that time about five thousand determinations of carbon have been run in this laboratory by that method, and this paper reports experience with it. The general problem of determining the carbon in iron and steel has been well discussed by Lundell, Hoffman, and Bright (*7*). In most general use for irons and steels is the combustion method (pp. 157 ff.), in which the steel is burned in a stream of oxygen and the resulting carbon dioxide is absorbed in a suitable train. There are many sources of error in this method, some of which are not easily controlled. These are reflected in the relatively large blank, which is difficult to reduce when dealing with small amounts of carbon and often equals or exceeds the amount to be determined. Measurement of the carbon dioxide formed by combustion of the steel has been one of the chief sources of error. It is upon this point in the procedure that many efforts (*6*) have been directed to reduce the error involved. Further comparisons of these methods are given below.

APPARATUS

The earliest form of the authors' apparatus is similar to Wooten and Guldner's and is shown in Figure 1 with Z joined to Z' and the intermediate traps omitted, and without the cutoff on the combustion vessel. Various modifications have been made of the equipment, which at the present time is used in the form shown in Figure 2. This form requires the use of only two mercury wells, thus reducing the amount of mercury required by a factor of 2. As mercury is a critical costly material at the present time, it is expected that the McLeod gage can be replaced by a Pirani gage for measuring the concentration of carbon dioxide produced, with a consequent saving in mercury and the convenience of a direct-reading instrument.

Although Figure 2 shows only a single unit, the authors actually construct four units to operate from a common oxygen supply system (Figure 3). A single auxiliary vacuum serves for all four, and whereas each unit requires one mercury diffusion pump, the units are joined to operate with a common fore pump. Four units are all a single operator can conveniently manage. Just outside the picture at the left, symmetrically arranged with respect to the oscillator, is another unit of four. Both receive their power from the 5-kilowatt oscillator shown behind the operator.

In describing the apparatus, manipulation, and results, only the differences from the procedures described by Wooten and Guldner are emphasized; their publication (*13*) should be consulted for the elaboration of details. To facilitate comparison between the two papers, the same symbols are used in Figures 1 and 2 to designate parts and equipment functionally the same.

PURIFICATION OF OXYGEN. The catalyst is contained in a Pyrex tube and it has not been necessary to use the quartz tube shown in Wooten and Guldner's apparatus. This catalyst is active enough at 400° C. to oxidize all the carbonaceous materials occurring in the authors' oxygen gas. The palladium black catalyst was prepared by the method described by Farkas and Melville (*3*, p. 338) by precipitation on broken pieces of Alundum and was loaded into the tube after preparation. Operation of the catalyst at this low temperature considerably lengthens the life of the furnace used to heat the tube. The amount of oxygen consumed is small; hence, the gas from an ordinary pressure cylinder will last a long time and is more constant in composition than line oxygen.

Although the authors use liquid nitrogen for cooling their traps, and liquefied the oxygen in their first experiments, they found that they could obtain oxygen of sufficient purity to give a low blank, simply by passing it in the gaseous state through the double traps. This technique simplifies operation of the equipment and permits liquid air to be used when liquid nitrogen is not available. The liquefaction of oxygen permits a larger amount of the gas to be stored ready for use, but a simple calculation of the amount of oxygen consumed by the burning iron, silicon, etc., in the sample shows that it is adequately supplied by the volume of gas trapped by the mercury when the level of mercury is at L_1. The substitution of stopcock S_2 for a mercury cutoff used in Wooten's apparatus has not raised the blank on the oxygen by any amount that will interfere with the determination. The grease used for this stopcock is Apiezon L.

COMBUSTION SYSTEM. The combustion chamber used for the earlier work permitted the insertion of only one sample into the system for each determination as shown in Figure 1. The sample dropped directly into the crucible before the side tube was sealed off. The disadvantages are, first, that air must be admitted to the system each time a determination is run; and the subsequent pumping and degassing are time-consuming. The air carries carbon dioxide and dust into the system, which may produce an increase in the blank. Secondly, the blank cannot be determined directly before the sample is run because of the presence of the iron sample in the crucible, and if air enters the system between the running of the blank and the running of the sample, it is not possible to ascertain whether the blank has been changed.

These difficulties were eliminated by the multiple loading system devised by Benjamin M. Walker of this laboratory, whose innovation speeded the operation of the method considerably and added to its precision. The diagrammatic arrangement of this loading tube is shown in Figure 2, and a photographic close-up is shown of one type of arrangement of the tubes holding the samples in Figure 4. The sample is held at a until a satisfactory blank has been obtained on the apparatus, and then is transferred by means of a magnet to the inclined glass tube, whence it is easily moved until it falls into the crucible. The number of such samples that can be sealed into the loading tube at any time is limited by the number that will fill the crucible, and this is dependent to some degree upon the type of sample used. The authors find that a crucible will take about 28 samples, and loading tubes hold 14 samples. The clinkers should not fill the crucible higher than to within 0.6 cm. (0.25 inch) of the top. When the crucible is thus filled it must be replaced by removing the top of the combustion vessel. In order to keep the equipment in continuous use, a duplicate combustion vessel with crucible and loading tubes with samples can be made ready and the complete combustion vessel units interchanged.

The platinum-iridium (0.4%) crucibles used were specially designed for the purpose by J. Bishop and Co., Malvern, Pa. They are of 15-ml. capacity and have welded to the rim a loop which allows the crucible to hang 9 cm. below the support in the combustion vessel. The platinum crucibles expand when heated, allowing the ceramic liner to slide down to a lower position which imposes a strain on the crucible when it cools to room temperature. The usual crucibles showed a tendency to crack around the upper rim, as well as about the bottom. The high-frequency current raises the point of such breaks to the melting point of platinum with disastrous results. By heavily reinforcing the bottom and the rim, this difficulty has been almost completely eliminated. At one time difficulty with high blanks was traced to a lot of crucibles which had apparently been contaminated by the formation of platinum carbide during manufacture. The blank could not be lowered by a cycle of repeated ignitions of the crucible in pure oxygen and pumping off to a low pressure, although the

process was repeated continuously for several days. Care should be exercised to get platinum free of carbon.

The first ceramic liner used for the platinum crucible consisted of a fused silica crucible, the bottom of which was covered with Alundum powder. The use of Alundum is objectionable because of the blank it introduces and the space it occupies in the crucible. The silica, being acidic, is readily attacked by molten iron oxide, forming a slag which shatters the crucible and destroys its usefulness. G. H. Porter of the ceramic laboratory prepared crucible liners high in magnesium oxide content. These proved very much more satisfactory and were eventually replaced by the magnesia liners described by Wooten and manufactured by Norton. Since that time Louise Harrop of this laboratory has prepared beryllium oxide crucibles which are even more satisfactory as liners, by a method similar to that outlined by Thompson and Mallett (*11*). Dr. Harrop's liners are slightly smaller in outside dimensions, permitting a thin layer of powdered beryllia to be placed between liner and crucible. This arrangement greatly facilitates the removal of the liner from the platinum crucible after it has been filled with combusted samples. The blanks obtained on beryllia liners seem to be lower than can be obtained on the magnesia. It is expected that beryllia liners of this type may become commercially available.

Analysis System. The pumping system consists of a two-stage mercury diffusion pump of the type shown by Dushman (*2*) and manufactured by the General Electric Co. Details of the construction are shown in his article (*2*). The speed of this pump is considerably greater than of single-stage pumps that have been used. As backing pump for four units the authors use a Welch two-stage Duo-Seal vacuum pump, Catalog No. 1405H. The pump for the auxiliary vacuum used to evacuate the chamber above the mercury in the mercury wells needs to be capable of going to only a few millimeters' pressure.

Single traps are often too inefficient to trap condensed carbon dioxide. The solid material may be blown through the trap by a flow of uncondensed gas. Attempts to prevent this by using a plug of glass wool in the traps made it exceedingly difficult to get a good vacuum. Consequently, this technique was abandoned in favor of the double traps shown in the diagram.

The large hollow stopcock, S_7, with 15-mm. bore is vacuum-tight, of excellent construction, and can be obtained from Eck and Krebs, New York, N. Y.

The highest percentages of carbon reported by Wooten (*13*) are approximately 0.02%. The authors wished to analyze samples of steel containing as high as 0.06% carbon. It is not easy to get a representative sample of steel less than 0.5 gram nor is it convenient to work with samples much smaller than 0.5 gram; hence, the authors added an auxiliary volume (Figure 2, $V' - V$) to their equipment, whose use is explained below.

They have used one 1.5-kva (output) Lepel Model C-3 high-frequency converter with a frequency range 170 to 500 kc. for four units. For more units they find it advisable to use more power and are now employing for eight units a General Electric 5-kva (output) power oscillator, Model 4F5A4, mean frequency 550 kc. The coil which surrounds the combustion vessel must be designed to conform with the characteristics of the oscillator. For each set of four units there is one coil. The two coils are connected in series and so to the oscillator. Air cooling must be provided to keep the walls of the combustion vessel from being overheated by radiation from the platinum crucible. The authors have used a small hand hair dryer clamped in a support or a jet of air from the laboratory compressed air system. An insulating casing, as of Herkolite, surrounding the high-frequency heater, is desirable to prevent the operator from actually touching the turns of the conductor. Although they are cold and a high-frequency current does not produce a shock, nevertheless an arc which will produce a deep burn can be drawn by accidental contact.

Calibrating the Volume. In this method the volume of the McLeod gage must be known. First ascertain that the system has no leaks and earn the time required to evacuate the system from 5- to 10-mm. pressure to 10^{-5} mm. (usually 10 to 15 minutes with mercury pump hot at the start).

Evacuate the system, holding the mercury down in both reservoirs. With pumps running, open S_8 momentarily, admitting a small mount of air to the system. Quickly raise the mercury in the McLeod gage, thus trapping air in the bulb and capillary of the gage. Run the mercury up in the gage and determine the pressure of this trapped gas. Thus a known volume of gas is obtained, V_1, at a measured pressure, P_1. (The volume of the bulb

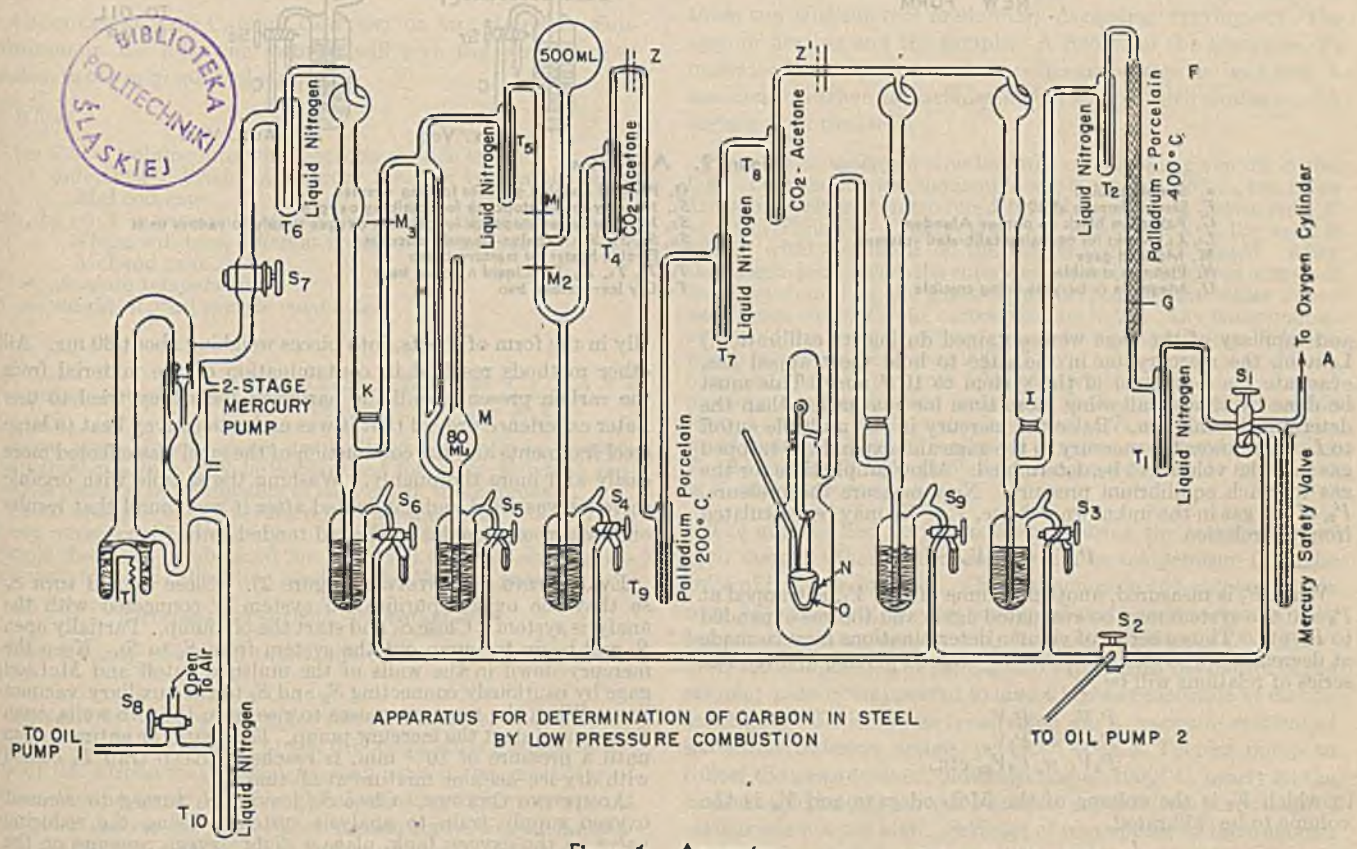
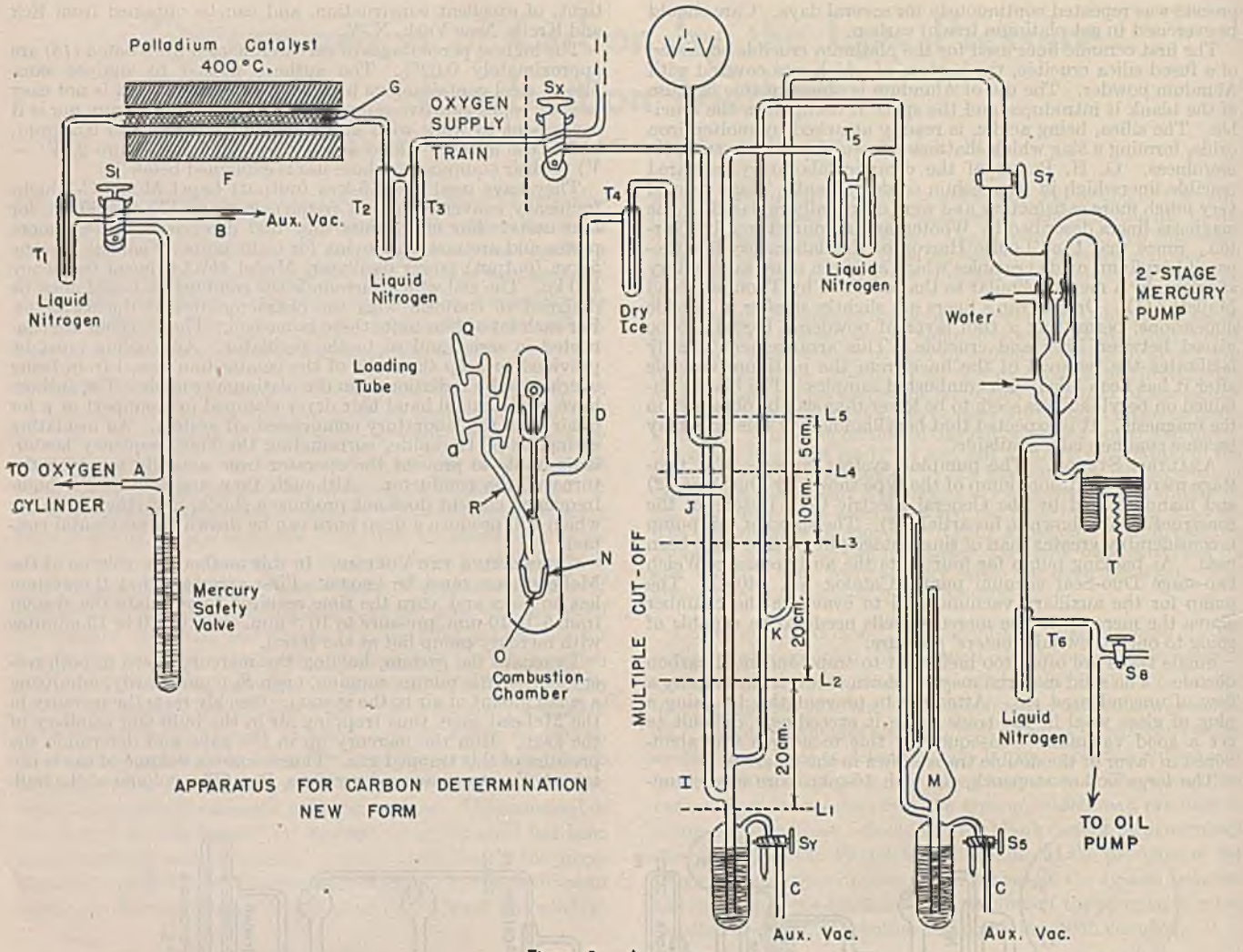


Figure 1. Apparatus

F. Electric furnace at 400° C.
G. Palladium black on porous Alundum
M. McLeod gage
M_1, M_2, M_3. Marks for confining calibrated volumes
N. Platinum crucible
O. Magnesia or beryllia lining crucible
S_1. Mercury-sealed stopcock for admitting oxygen
S_2, S_3, S_4, S_5, S_6, S_7, S_8, S_9. Precision-ground stopcocks
T. Electric heater for mercury pump
T_1, T_2, T_3, T_6, T_7, T_{10}. Liquid nitrogen traps
T_4, T_5. Dry ice–acetone traps
T_8. Trap filled with palladium black on porous Alundum
Z, *Z'*. Extra equipment for separating H_2, H_2O, CO, and CO_2



APPARATUS FOR CARBON DETERMINATION
NEW FORM

Figure 2. Apparatus

a. Sample pocket
F. Electric furnace at 400° C.
G. Palladium black on porous Alundum
L_4, L_5. Marks for confining calibrated volumes
M. McLeod gage
N. Platinum crucible
O. Magnesia or beryllia lining crucible
Q. Point of opening glass for loading samples
S_1. Mercury-sealed stopcock for admitting oxygen
S_x. Mercury-sealed stopcock for dividing oxygen supply to various units
S_y, S_5, S_7, S_8. Precision-ground stopcocks
T. Electric heater for mercury pump
T_1, T_2, T_3, T_5, T_6. Liquid nitrogen traps
T_4. Dry ice–acetone trap

and capillary of the gage were obtained during its calibration.) Leaving the mercury up in the gage to hold the trapped gas, evacuate the remainder of the system to 10^{-5} mm. This must be done by timing, allowing more time for evacuation than the determined minimum. Raise the mercury in the multiple cutoff to L_5, then lower the mercury in the gage and expand the trapped gas into the volume to be determined. Allow ample time for the gas to reach equilibrium pressure. Now measure the pressure, P_2, of the gas in the unknown volume, V_x. V_x may be calculated from the relation

$$P_1V_1 = P_2V_x$$

When P_2 is measured, another volume of gas, V_1, is trapped at P_2 and the system may be evacuated again and the gas expanded to P_3, etc. Thus a series of volume determinations may be made at decreasing pressures from the one original portion of air. The series of relations will be

$$P_1V_1 = P_2V_x$$
$$P_2V_1 = P_3V_x$$
$$P_3V_1 = P_4V_x, \text{ etc.}$$

in which V_1 is the volume of the McLeod gage and V_x is the volume to be calibrated.

PROCEDURE FOR ANALYSIS

The preparation of the steel is the first important step in the analysis. The authors expected to have to reduce the steel to a finely divided powder in order to ensure complete combustion, but they were unable to do better than cut the silicon steel, usually in the form of sheets, into pieces weighing about 30 mg. All other methods resulted in contamination of the material from the carbon present in all the hardened tools they tried to use. Later experience proved that it was easier to convey heat to large steel fragments and the combustion of the steel was effected more easily and more thoroughly. Washing the sample with organic solvents was tried and eliminated after it was found that results on low-carbon samples so treated tended to be high.

Evacuating the System (Figure 2). Close S_1 and turn S_x so that the oxygen-purification system is connected with the analysis system. Close S_7 and start the oil pump. Partially open S_7 and begin to pump out the system from S_1 to S_7. Keep the mercury down in the walls of the multiple cutoff and McLeod gage by cautiously connecting S_y and S_5 to the auxiliary vacuum line. When the mercury ceases to rise from the two wells, open S_7 wide and start the mercury pump. Evacuate the entire system until a pressure of 10^{-5} mm. is reached. Keep trap T_4 cooled with dry ice–acetone mixture at all times.

Admitting Oxygen. Close S_7, leaving S_x turned to connect oxygen supply train to analysis system. Using the reducing valve on the oxygen tank, place a slight oxygen pressure on the line from A to S_1 (this pressure will be indicated on the mercury safety valve). Raise the mercury in the multiple cutoff to L_1 by admitting air through S_y, and in the McLeod gage to the level of the cutoff arm of gage M by admitting air through S_5. By opening S_1 slightly and maintaining a pressure from the tank, admit oxygen to the system until a pressure of about 15 to 20 cm.

has been attained. This pressure will be indicated by the mercury dropping back into the wells of the multiple cutoff and McLeod gage. The mercury safety valve serves to prevent excess pressure on the system from the tank, and also gives a visual indication of pressure which helps in adjusting S_1 and the tank reducing valve while oxygen is being admitted. By constant adjustment of S_1 and the tank reducing valve, the mercury can be kept level in the safety valve and gas admitted to the system without difficulty. When an oxygen pressure of 15 to 20 cm. has been attained in the system, raise the mercury in the multiple cutoff to L_3 and connect S_1 to the auxiliary vacuum. Pump out the excess oxygen until the mercury ceases to rise in tube I, then close S_1 and S_x.

Burning the Sample. By manipulation with a small Alnico magnet, move the sample through R into the crucible. Heat the platinum crucible to 1200–1300° C. Direct a stream of air from a fan or compressed air line onto the combustion chamber to cool the glass. As soon as the crucible reaches maximum temperature, the sample will oxidize (if the silicon content is high enough it will burn), but the crucible is kept hot for 15 minutes longer to ensure complete combustion of the carbon. While the sample is burning, place liquid nitrogen around T_5. After combustion is complete, carefully open S_7 just enough to raise the mercury in tube K, so that it is level with the mercury in the two tubes to the left of K (the difference in levels is caused by the oxygen used in the combustion). Lower the mercury in the multiple cutoff to L_2 and open S_7 slightly. This begins the removal of the excess oxygen while the carbon dioxide is frozen out in T_5. The mercury will rise slowly in the multiple cutoff, but must be kept below K. When the mercury ceases to rise, column I will again be level with the others. Open S_7 wide and pump the system until a pressure of 10^{-5} mm. is reached. When the system is evacuated, raise the mercury to L_5 and close S_7. Expand the carbon dioxide into V by removing the liquid nitrogen and allowing T_5 to come to room temperature. Measure the pressure of the gas on the McLeod gage, or if the pressure is too high to read in the small volume, lower the mercury to L_4 and take the pressure on the larger volume, V'.

After having obtained the pressure of the carbon dioxide, lower the mercury to L_1 and evacuate the system to a pressure of 10^{-5} mm. before admitting oxygen for the next sample.

Calculating the Carbon Content of the Sample. Substitution in the following formula will give the percentage of carbon in the original steel sample.

Where

V (or V') = volume into which carbon dioxide expands
h = difference in height of mercury levels in two capillaries of McLeod gage
$k(k_1, k_2$, etc.) = constants for converting h to absolute pressure There will be a different constant for each mark on the McLeod gage.
T = absolute temperature
w = weight of steel sample combusted

then,

$$\text{Percentage of carbon} = \frac{100 \times 0.2729 \times 273 \times 44 \times V \times h \times k}{760 \times 22{,}400 \times w \times T}$$

Since some McLeod gages are calibrated directly in pressure the actual pressure may be substituted for $(h \times k)$ which represents pressure in millimeters of mercury in this expression.

Small changes in temperature do not affect the value of the above expression appreciably. Therefore, for a fixed weight of sample there can be obtained for V (or V') a simple series of expressions for each calibration mark on the McLeod gage:

$$\text{Percentage of carbon} = \text{constant} \times h$$

This is easily converted to a graphical form for quick calculation.

Sensitivity. Since the difference in height of the mercury levels in the two capillaries of the McLeod gage is the final measure of the carbon in the steel, we may express the sensitivity of this method in terms of the height of mercury which corresponds to a given carbon content. When measuring carbon contents in the range 0.02 to 0.03%, using a 0.5-gram sample and expanding the carbon dioxide into the smaller volume, V, a difference of 10 mm. in the heights of the mercury columns at the highest reading range of the McLeod gage (lowest sensitivity) corresponds to 0.001% carbon. When reading the lowest pressures on the McLeod gage, a difference of 10 mm. corresponds to 0.00006% carbon. Obviously the sensitivity of the method increases with decreasing carbon contents. The inherent limitations which the authors have found in determining carbon arise not from the sensitivity of the measurement, but from the lack of uniformity in the distribution of carbon. The reproducibility found, working with samples in which the carbon content is seldom below 0.004%, permits fixing the carbon content within ±0.0005%. For this reason the authors have been content to work with a larger blank than Wooten and Guldner. In general the blank averages 0.0005%. The blank has not been subtracted from any of the results reported in this paper.

When operations are started for the day, even when the apparatus has stood overnight under high vacuum, there is a high blank, usually 0.001% or higher. After running one sample of steel, the blank drops and, in general, continues low throughout the day. The authors can find no explanation for this phenomenon. Actual results are further discussed below.

Combustion of Sample. The combustion of a steel sample of high silicon content will consume about 600 ml. of oxygen measured at 20° C. and 200 mm. pressure, assuming that the iron is oxidized to Fe_3O_4 and the silicon to silica. Since the supply of oxygen is not in equilibrium with the liquid phase but is shut off from the supply before combustion starts, the pressure falls by about 70 to 80 mm. during the combustion. No difficulty seems to have been raised by this change in technique. The composition of the clinker remaining as a residue has been shown to be chiefly Fe_3O_4 by the x-ray diffraction method.

In the earliest analyses, the sample after being introduced into the crucible was heated to about 500° C. for 5 minutes to drive off any adsorbed gases, particularly any that might contain carbon before oxygen was admitted. Results obtained from samples treated in this fashion were lower by about 0.001 to 0.01% than those run without this preliminary degassing, varying with the time of heating and the sample. A review of the literature (*5*) indicates that any such carbonaceous gases were derived from a reaction of carbon or carbides in the sample with oxides on the surface or in the steel.

In order to ascertain whether any carbon was given off in the form of monoxide when the sample was heated to 500° C., two traps and a catalyst were introduced into the system as shown from Z to Z' in Figure 1. The system was evacuated and the sample heated with the cutoff on the combustion vessel closed. After the sample had cooled, the cutoff was opened and oxygen admitted to the system. As the gases were pumped off, the water vapor was frozen out in T_8, the carbon dioxide in T_7. Any carbon monoxide and the residual oxygen passed over the palladium catalyst which was maintained near 200° C. by a boiling bath of trichlorobenzene. Any water from hydrogen which might have escaped previous combustion was frozen out in T_4. The carbon dioxide formed over the catalyst was frozen out in T_5 and measured in the usual manner. This gas is allowed to escape and then by warming T_7 the carbon dioxide previously condensed there is frozen out in T_5 and measured.

The authors had no means for measuring the temperature of their sample, other than of estimating the temperature from the color of its incandescence. Carbon monoxide and carbon dioxide were both evolved; the proportion of the former increased with temperature in agreement with the results of Ryder (*8*). However, the composition of the gas also varied with the nature of the sample; pure iron appeared to give a higher proportion of carbon monoxide. Experiments conducted in a vacuum system of somewhat different design, provided with a Toepler pump to collect the gases evolved, indicated that at 1000° C. nearly all the carbon could be driven from a sample, provided the percentage of carbon was not too high. Samples of iron appear to have enough oxide on the surface or internally to bring about this oxidation. Since heating can remove an appreciable amount of carbon from the sample, the preliminary heating was dropped and the sample combusted without "degassing" the sample at an elevated temperature.

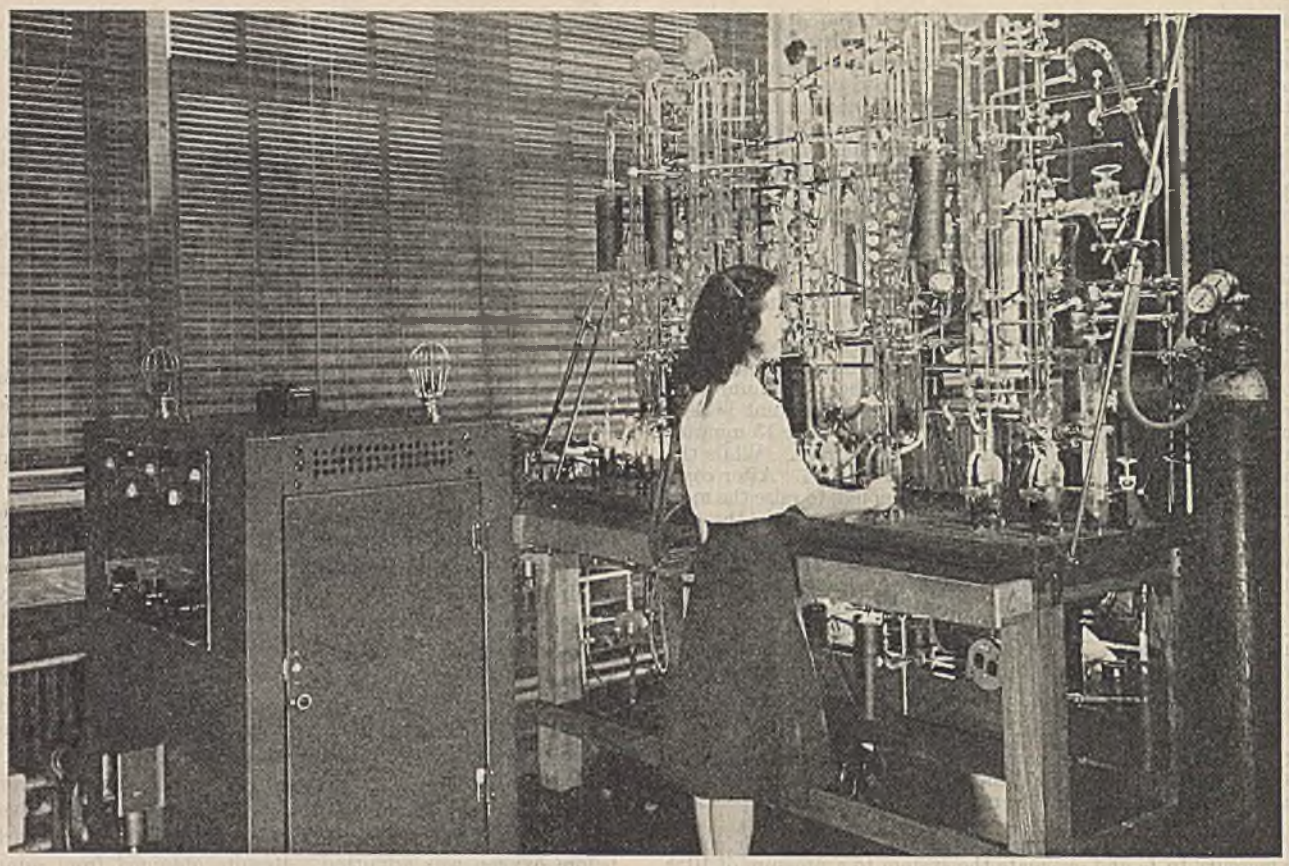


Figure 3. Low-Pressure Combustion Apparatus in Pittsfield Laboratory

No evidence of the incomplete oxidation of carbon to carbon dioxide when a sample is burned was found with the arrangement of apparatus in Figure 1.

When the platinum crucible is heated in the evacuated combustion vessel, no deposit is formed on the walls of the vessel. When oxygen is present, the wall becomes brown, then gradually black and opaque. The deposit, when scraped off and examined by testing its diffraction of x-rays, is shown to be platinum metal with some iron oxide (Fe_3O_4). Since this deposit forms only when oxygen is in the system, the intermediate formation of platinum oxides seems not improbable (*9*).

RESULTS

In order to demonstrate the agreement that is possible with this method between various laboratories and different operators, the authors have compiled the data shown in Table I. They are indebted to J. B. Austin of the United States Steel Research Laboratory for the use of their data. Each "series" was run on one or more different apparatus or on apparatus completely dismantled and rebuilt. The data have been obtained over a fairly long period of time. The results grouped as "I Pittsfield G. E. (3 operators)" were accumulated over many months and on more than one apparatus. The operators included high-school graduates as well as chemists with postgraduate training.

The summary attempts to show how these six averages compare with the thirteen reported on the Bureau of Standards certificate for sample 55a. These results were obtained by selected cooperators who (with one exception) used the classical combustion method. After preliminary results are submitted by cooperators, the bureau customarily requests additional tests when reports deviate too grossly from the mean.

The results reported for the low-pressure combustion method represent all those obtained with the three exceptions noted. The elimination of the six values as indicated in Table I does not affect the mean of the six averages appreciably. The spread of the six averages reported is 0.0014% (Table II) compared with 0.004% for the bureau's cooperators. The average deviation is ±0.0006% compared with 0.001% (the fourth decimal place is not reported on the bureau certificate, hence this comparison is not strictly fair).

Table I. Summary of Results for Carbon Analysis

(Bureau of Standards Sample 55a)

Series	Reported by	No. of Determinations	Average, %	Average Deviation $\times 10^3$	Spread Highest-Lowest $\times 10^3$	Standard Deviation, $\sigma \times 10$
1	Bell Telephone Laboratories (*13*)	10[a]	0.0108	0.1	0.4	0.1
2	II Brackenridge G. E. (E. J. Fitz)	8	0.0109	0.4	1.1	0.4
3	I Brackenridge G. E. (E. J. Fitz)	11[b]	0.0109	0.2	0.8	0.3
4	U. S. Steel Corp. (J. B. Austin)	10[b]	0.0116	0.2	0.8	0.2
5	I Pittsfield G. E. (3 operators)	10[b]	0.0121[c]	0.3	1.3	0.4
6	II Pittsfield G. E. (L. Casali)	12	0.0122[c]	0.4	1.9	0.5
	Unweighted mean of six averages		0.0114			

[a] Including additional value, 0.0110, sent by Wooten.
[b] After rejecting two values whose deviation from mean exceeds four times average deviation of rest of group.
[c] Averages in 5 and 6 on different samples of standard 55a.

Table II. Carbon Analysis

(Comparison of six averages of Table I with thirteen averages reported on B. of S. certificate 55a)

	% Carbon	Mean Deviation of Averages $\times 10^3$	Spread $\times 10^3$ (Highest-Lowest)	Values Reported
Recommended value B. of S. certificate	0.014	1.0	4.0	13
Mean of averages (Table I)	0.0114	0.6	1.4	6

Table III. Carbon in 3% Silicon Steel, Sample A

Determined Carbon Value			
29 Determinations Run on Eight Units at Pittsfield (3 Operators)		21 Determinations Run on Four Units at Brackenridge (3 Operators)	
%	%	%	%
0.0034	0.0027	0.0027	0.0042
0.0029	0.0035	0.0023	0.0035
0.0027	0.0029	0.0036	0.0029[a]
0.0027	0.0028	0.0027[a]	0.0026[a]
0.0032	0.0040	0.0027[a]	0.0038[a]
0.0034	0.0040	0.0030[a]	0.0029[a]
0.0026	0.0041	0.0038	0.0035
0.0029	0.0034	0.0033	0.0026
0.0028	0.0032	0.0026[a]	0.0032
0.0031	0.0028	0.0033[a]	0.0029[a]
0.0033	0.0031	0.0042	
0.0031	0.0029		
0.0035	0.0027		
0.0033	0.0031		
0.0031			
Av. 0.0031		Av. 0.0032	
Average deviation ±0.0003		±0.0005	
Standard deviation ±0.0004		±0.0005	

[a] High-carbon samples interspersed with these runs.

Table IV. Carbon in 3% Silicon Steel, Sample B

Standard combustion value, 0.006% carbon. Eight units, two operators.

Date	Unit	Percentage Carbon: Blank (before)	Value	Blank (after)
		Portion *A*, *n* = 11		
12-4-43	A	0.0010	0.0036	0.0006
12-4-43	C	0.0006	0.0046	0.0007
12-4-43	D	0.0006	0.0043	0.0006
12-6-43	A	0.0006	0.0040	0.0006
12-6-43	C	0.0007	0.0042	0.0011
12-7-43	D	0.0009	0.0038	0.0006
12-14-43	B	0.0005	0.0043	0.0006
12-14-43	C	0.0005	0.0041	0.0007
12-14-43	D	0.0008	0.0051	0.0009
12-15-43	B	0.0006	0.0044	0.0006
12-15-43	B	0.0006	0.0048	0.0007
		Av.	0.0044	
		Standard deviation	±0.0004	
		Portion *B*, *n* = 9		
12-20-43	E	0.0009	0.0036	0.0004
12-23-43	E	0.0004	0.0050	0.0008
12-23-43	F	0.0005	0.0036	0.0005
12-23-43	G	0.0004	0.0042	0.0005
12-29-43	F	0.0004	0.0041	0.0006
12-29-43	G	0.0006	0.0041	0.0005
12-29-43	H	0.0007	0.0037	0.0006
1-8-44	B	0.0005	0.0042	0.0007
1-11-44	B	0.0005	0.0038	0.0007
		General av. 0.0006₂	Av. 0.0040	General av. 0.0006₂
		Standard deviation	±0.0004	

The most striking feature of the comparison is the fact that the average by the method under discussion is 0.011% compared with 0.014% reported by the bureau certificate. In general, it has been the authors' experience that their results by this method on Bureau of Standards samples containing up to 0.3% carbon average a few thousandths of a per cent lower than the certificate values which are usually obtained by the classical combustion method. It is their opinion that occasional "wild" values obtained on even a carefully prepared well-mixed sample of steel come from a lack of uniformity in the distribution of carbon in the sample. It becomes evident with this method because of the small size of samples taken for chemical analysis.

Finally, series 2, 3, and 6 obtained by the authors' operators show somewhat poorer consistency than series 1 and 4. This probably reflects the effort to reduce the time required per determination and represents a slight sacrifice of accuracy in favor of speed. This is further discussed below.

In Tables III and IV are given typical sets of data to show the reproducibility that may be obtained with 3% silicon steel. All data over a given period of time are reported in both tables, with the exception of one very high value on portion A, Table IV. The precision of the authors' method seems to be consistent as measured by the standard deviation reported in Tables I, III, and IV.

Table V. Analysis of High-Manganese (14.4%) Iron Alloy

Before Treatment: Wt. of sample	Carbon, sample I	After Treatment: Wt. of sample	Carbon, sample II
Gram	%	*Gram*	%
0.05	0.0206	0.05	0.6191
0.1	0.0178	0.05	0.6502
0.2	0.0155	0.1	0.6780

Carbon Determined		versus	Carbon by Weight Increase	
Sample II, % C after treatment	0.649		Sample II, % gain in weight	0.65
Sample I, % C before treatment	0.018		Sample II, % B added by treatment	0.02
Carbon added by treatment	0.631		Gain in weight corrected for B	0.63

A difficult question to settle in the determination of carbon is whether all the carbon is removed from the sample in the course of a combustion. In Table V are shown the results obtained in the recovery of carbon.

Two samples of high-manganese iron wire with weights shown were submitted by H. H. Uhlig of the G. E. Research Laboratory in Schenectady, who had observed a gain in weight under treatment which could be attributed to boron or carbon (lower right column). These data were not known to the authors at Pittsfield, and the carbon found by combustion was reported as given in the two upper columns. Boron was found in the wire, hence the gain in weight due to carbon is shown in the lower right column. This checks well with the authors' analysis. The spread in their carbon values in the upper two columns may be attributed to ununiform distribution of carbon as well as to the difficulty of completely burning the sample.

DISCUSSION

The time required for a determination by this method as described by Wooten and Guldner is not stated in their paper. The authors found that with the apparatus described, consisting of a single unit with one operator, a determination averaged about 2 hours, though under exceptional circumstances they have been able to average about one determination per hour through a single 8-hour day. A single operator can, however, manage about four units, provided he does not prepare and weigh the samples. With an assistant to prepare the samples, it is possible on the present equipment to average a single determination every half hour. A set of four units such as the authors have been using about 2 years is shown in Figure 3. Their experience has indicated that intelligent high school graduates can operate this equipment satisfactorily under the guidance of technically competent college graduates. When large amounts of data must be accumulated for statistical studies or production control, time and cost factors must be considered and will determine the feasibility of the analytical method.

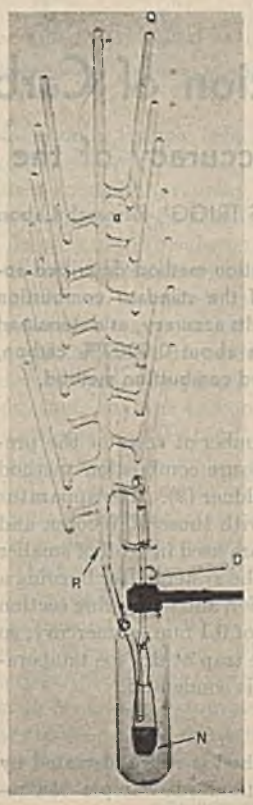


Figure 4. Combustion Chamber, Showing Multiple Loading System

The authors have attempted to adapt some of the older methods for carbon determinations. When the carbon and carbides are first separated by dissolving the steel in potassium copper chloride (7, p. 179) the amount of carbon recovered varied directly with the time the sample was centrifuged. Appar-

Table VI. Carbon Content of Pure Copper

	Carbon	
	Specimen A	Specimen B
	%	%
Sample I	0.0017	0.0015
Sample II	0.0016	0.0025
	Av. 0.0017	0.0020

ently some of the carbon separates in a form which tends to remain in suspension and is filtered off on sintered glass only with difficulty.

The barium hydroxide method (*7*, p. 172) has been tried, but with the type of absorber shown in Figure 39 (*7*, p. 173) it seemed impossible to get complete absorption of the carbon dioxide with any reasonable adjustment of oxygen flow, concentration of barium hydroxide, etc. (*1*). It is, therefore, necessary to use an empirical factor in calibrating the standard solution for this method, and the factor will change with any of a number of variable circumstances. The method does not recommend itself to the determination of small amounts of carbon. Attempts to improve the efficiency of absorption and to finish the analysis gravimetrically usually result in increasing the length of the method to an inconvenient degree (*12*). Good results were reported by Thanheiser and Dickens (*10*) using barium hydroxide as an absorbent for iron and steel containing a few thousandths of a per cent carbon. However, large samples of about 10 grams are required to secure the desirable accuracy, and, when the size of the sample is decreased, there is a correspondingly large decrease in the accuracy of the results.

CARBON IN COPPER

The only values given in the literature for the solubility of carbon in copper are those of Floe and Chipman (*4*). The authors were asked to determine the carbon content of a sample of high-purity copper prepared in the laboratory by melting in a graphite crucible under an atmosphere of nitrogen. When copper oxidizes, the heat of the reaction is less than for the oxidation of iron, and the copper does not burn. However, it is possible to oxidize it completely under the conditions described above for iron. The results on two samples of copper prepared as just described are shown in Table VI.

ACKNOWLEDGMENT

Thanks are due to many within and without the authors' organization for cooperation, criticism, and suggestions in achieving the results shown in this paper. Particularly they wish to thank Benjamin M. Walker and Miss Liberty Casali for suggestions and for assistance in running many hundreds of determinations.

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Determination of Carbon in Low-Carbon Steel

Precision and Accuracy of the Low-Pressure Combustion Method

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The precision of the low-pressure combustion method described appears to be at least three times that of the standard combustion method when used on low-carbon steel. Its accuracy, as determined by direct calibration on Iceland spar, is about 0.0007% carbon, again about three times that of the standard combustion method.

THIS paper reports the results of a number of tests of the precision and accuracy of the low-pressure combustion method for carbon described by Wooten and Guldner (*2*). The apparatus and procedure are virtually identical with those of Wooten and Guldner, except that large single traps are used instead of smaller double ones, and during evacuation of the system after burning a sample the U-seal between the combustion and measuring section of the apparatus is closed at a pressure of 0.1 mm. of mercury, so that water may not be carried from the trap at dry ice temperature to the one in which carbon dioxide is condensed.

PRECISION

The precision attainable by this method is well illustrated by the analyses of National Bureau of Standards Sample 55a reported by Murray and Ashley (*1*, Table I). The authors have also investigated the precision relative to that of the common combustion method on four samples of steel, which proved to range in carbon content from 0.015 to 0.026%. These were submitted for analysis to four laboratories which use the ordinary combustion method, all accustomed to analyzing steels of this type, so that the results which each reports may be assumed to be reasonably representative of the precision that his procedure is capable of yielding. These results are given in Table I, columns A to D; the authors' results by the low-pressure method are in column E.

For each laboratory the mean for each sample was calculated and the deviation, Δ, from this mean tabulated; for the sake of clarity these deviations have all been multiplied by 1000. The average deviation from the mean for all samples done by each laboratory was calculated from the arithmetic sum of the individual deviations—that is, without regard to the sign of each. This average is a measure of the precision of the analysis reported by each laboratory.

On the basis of these data, it is concluded that the precision of the low-pressure method is in general about ±0.0005% carbon, although under favorable circumstances it may approach the value of the blank (about 0.0002), and that it is at least three times as good as that of the ordinary combustion method.

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The authors' general experience with the low-pressure method, in which a 0.5-gram sample is used, leads them to believe that there may be actual differences in carbon content of samples nominally identical unless they are prepared and handled with meticulous care; consequently the precision of the result may be limited less by that of the method than by the reproducibility, with respect to actual carbon content, of the sample analyzed.

ACCURACY

The accuracy of a method of analysis can be gaged in three ways: (1) by comparison of the results with those of other methods; (2) by analysis of a standard sample whose composition has been determined by a number of different analysts, preferably using different methods; or (3) by analysis of a suitable pure compound, the composition of which is fixed and reproducible. All three methods have been used in the present case.

An indication of the accuracy of the low-pressure method relative to that of the common combustion method can be derived from Table I by comparing the results of the several analysts with a grand weighted average. In doing this the question always arises as to who decides how the weighting is to be done. The authors have followed an impersonal procedure, frequently used, in which to each average is attached a weight inversely proportional to the average deviation from the mean of the individual results from which that mean was derived. Analyzing the data in Table I on this basis, they multiply for each sample the mean for each laboratory by the appropriate weighting factor (the reciprocal of the average deviation), and divide the sum of these products by the sum of the weighting factors (here 6.88). The resulting grand average is given here:

	Average Deviation × 1000 (from Table I)	Weighting Factor	Grand Weighted Average for Samples I	II	III	IV
A	0.8	1.25				
B	0.9	1.11				
C	1.4	0.71	0.0186	0.0151	0.0214	0.0261
D	2.1	0.48				
E	0.3	3.33				
		6.88				

The deviation of each laboratory's mean from the grand weighted average for each sample is shown in Table II. The mean deviation shown at the bottom of the column for each laboratory was derived by dividing the algebraic sum of the deviations for the four samples—that is, with consideration of the sign of each—by four. This mean deviation from the grand weighted average not only indicates the accuracy of a particular laboratory, but also shows whether that laboratory tends to report high or low values. On this basis, the low-pressure method has an accuracy of twice to ten times that of the usual combustion method as carried out by the various laboratories.

As regards the second method of calibration, it was believed at first that a Bureau of Standards sample would provide a suitable standard. Accordingly, the authors selected Sample 55a, the certified carbon content of which is 0.014%, although the values reported by the laboratories which cooperated with the bureau in standardizing this sample ranged from 0.012 to 0.016%. Later they found that several other laboratories which use the low-pressure method likewise had been using this sample as a standard. The results of all these determinations are summarized by Murray and Ashley (*1*) and range from 0.0108 to 0.0122% with a mean of 0.0114, which is significantly lower than the certificate value, though just at the lower limit of the range covered by the bureau's collaborators. The authors' general experience indicates that analyses made by the low-pressure method commonly yield a carbon content slightly lower than that obtained by the ordinary combustion method. The determinations of carbon in Sample 55a, instead of providing the desired check on the accuracy of the low-pressure method, have rather cast doubt upon the accuracy of the certificate value which should certainly now be reconsidered.

Table I. Comparison of Carbon Determinations

(By four laboratories and by the present procedure, on four samples of steel. The deviation, Δ, in each case is the deviation × 1000 from the mean obtained for each sample by that laboratory.)

No. of Sample	Standard Procedure in Laboratory A %	A Δ	B %	B Δ	C %	C Δ	D %	D Δ	Low-Pressure Method E %	E Δ
I	0.019	0	0.016	−1	0.025	−1	0.028	+4	0.0165	−0.2
	0.018	−1	0.016	−1	0.020	−6	0.028	+4	0.0162	−0.5
	0.020	+1	0.014	−3	0.024	−2	0.027	+3	0.0173	+0.6
	0.034[a]	...	0.020	+3	0.032	+6	0.015	−9	0.0171	+0.4
	0.031[a]	...	0.018	+1	0.027	+1	0.024	0	0.0166	−0.1
	....	...	...	...	...	...	0.023	−1	0.0164	−0.3
Mean	0.019_0		0.016_8		0.025_6		0.024_2		0.0167	
II	0.011	−3	0.012	+1	0.011	−1	0.019	0	0.0170	−0.1
	0.014	0	0.012	+1	0.011	−1	0.017	−2	0.0169	−0.2
	0.015	+1	0.010	−1	0.011	−1	0.017	−2	0.0175	+0.4
	0.016	+2	0.011	0	0.013	+1	0.025	+6	0.0171	0
	0.013	−1	0.011	0	0.012	0	0.018	−1	0.0173	+0.2
	0.014	0	...	...	...	...	0.018	−1	0.0169	−0.2
Mean	0.013_8		0.011_2		0.011_6		0.019_0		0.0171	
III	0.020	0	0.024	−1	0.023	0	0.018	−2	0.0200	−0.5
	0.020	0	0.026	+1	0.022	−1	0.020	0	0.0199	−0.6
	0.019	−1	0.026	+1	0.023	0	0.021	+1	0.0217	+1.2
	0.019	−1	...	...	...	...	...	...	....	...
	0.020	0	...	...	...	...	...	...	....	...
	0.022	+2	...	...	...	...	...	...	....	...
Mean	0.020_0		0.025_8		0.022_7		0.019_7		0.0205	
IV	0.026	0	0.024	0	0.029	0	0.027	0	0.0260	0
	0.026	0	0.024	0	0.030	+1	0.027	0	0.0256	−0.4
	0.027	+1	0.024	0	0.029	0	0.028	+1	0.0264	+0.4
	0.027	+1	...	...	...	...	...	...	....	...
	0.027	+1	...	...	...	...	...	...	....	...
	0.026	0	...	...	...	...	...	...	....	...
Mean	0.026_8		0.024_0		0.029_3		0.027_3		0.0260	
Average deviation		0.8		0.9		1.4		2.1		0.3
Maximum deviation		3		3		6		9		1.2

[a] Not included because deviation is so much greater than in all other results of laboratory A.

Table II. Deviation (X 1000) of Weighted Mean from Average of Laboratory

Sample	A	B	C	D	E (Low-Pressure Method)
I	+0.4	−1.8	+7.0	+5.6	−1.9
II	−1.3	−3.9	−3.5	+3.9	+2.0
III	−1.4	+3.9	+1.3	−1.7	−0.9
IV	+0.4	−2.1	+3.2	+1.2	−0.1
Av. (% C)	−0.0005	−0.0010	+0.0020	+0.0022	−0.0002

In view of the results on Sample 55a, special attention was paid to the third method of calibration, which was an absolute determination of the amount of carbon dioxide evolved from a crystal fragment of pure calcium carbonate (Iceland spar). A small crystal of analytical grade Iceland spar, carefully weighed on a microbalance, was placed in the magnesia crucible, oxygen was admitted, and the carbon dioxide determined by the standard procedure, special attention being paid to the rate of heating. The temperature of the crucible was raised from about 600° to 1100° C. over a period of about 20 minutes, after which it was maintained at this temperature for another 20 minutes before the carbon dioxide was collected.

The results of four such analyses (Table III) indicate that the average deviation of the observed amount of carbon dioxide from that calculated is 0.03×10^{-5} mole of carbon dioxide, equivalent to 0.0036 mg. of carbon, which for a 0.5-gram sample corresponds to 0.0007% carbon. On this basis, therefore, so long as the gas finally measured is substantially pure carbon dioxide, the accuracy of the method seems to be of the same order as its precision, since the average deviation shown in Table I is 0.0003% carbon.

COMPOSITION OF GAS COLLECTED

Before one can claim for the analysis of a steel the accuracy indicated by the evolution of carbon dioxide from Iceland spar,

Table III. Absolute Standardization with Iceland Spar (Calcium Carbonate)

$CaCO_3$	Weighed on	CO_2 Evolved (Pressure in Volume 251.9 Ml.)	Temperature	Carbon Dioxide Observed	Carbon Dioxide Calculated[a]	Carbon Dioxide Difference
Mg.		*Mm.*	° *C.*	*Mole*	*Mole*	*Mole*
1.9	Analytical balance	1.460	30	1.95×10^{-5}	$1.9_6 \times 10^{-5}$	$+0.0_4 \times 10^{-5}$
1.04_2	Microbalance	0.784	29	1.05	1.04	+0.01
1.25_0	Microbalance	0.918	28	1.23	1.25	−0.02
1.93_6	Microbalance	1.393	28	1.87	1.93	−0.06
					Mean	0.03

[a] 0.5 gram of steel containing 0.05% carbon gives 2.08×10^{-5} mole CO_2.

it is necessary to show that the material collected in the liquid nitrogen trap contains nothing other than carbon dioxide. That this is in fact true has been demonstrated by analysis of the condensed material by means of a fractional vaporization method based upon the fact that, as the temperature of the trap is slowly raised, there is for each condensed substance a characteristic temperature at which it vaporizes to cause a marked increase in the gas pressure of the system.

To carry out such a test, the trap was fitted with a copper shield, which helped to equalize the temperature, to which was attached a thermocouple. After combustion of a sample the excess oxygen was evacuated and the mercury levels were raised to isolate the calibrated volume. The trap was then quickly surrounded by an empty Dewar vessel which allowed it to warm only very slowly, and at suitable intervals the pressure was measured by means of the McLeod gage. For the materials condensed from the combustion of Bureau of Standards Sample 55a, which contained 0.02% sulfur and might have been expected to yield a little sulfur dioxide, the result of these measurements is shown by curve *A*, Figure 1.

The pressure, hence the number of moles of gas in the system, remained low up to about −120° C., at which temperature there was a relatively sudden increase to a pressure corresponding to the production of about 4.5×10^{-6} mole of gas; further increase of temperature up to 0° C. produced no further significant increase in the amount of material vaporized. The corresponding behavior of the condensate from the Iceland spar is shown by *B*, Figure 1. Had any sulfur dioxide or trioxide, or any other condensable substance, been present there would have been at a somewhat higher temperature another knee in these curves, as Wooten demonstrated by intentionally adding a little sulfur dioxide to the system.

Curve *A* indicates a slight evolution of gas between 0° C. and room temperature, an increase which is not evident in *B*. This increase, which was noted in all such runs on steel, indicates the evolution of less than 2% of some other gas, presumably water vapor. It is evident therefore that the gas condensed in the trap during combustion of a steel is virtually pure carbon dioxide.

The authors have also investigated the influence of two steps in the procedure upon the accuracy of the result. The first is the matter of washing the sample to remove superficial dirt and grease, which must be taken into account, since the surface of the sample is usually large and may therefore hold a relatively large quantity of carboniferous material.

If the sample is in the form of a thin strip, the surface can be cleaned by abrasion, after which the metal can be cut into small pieces with a pair of snips, avoiding any contact of the sample with the fingers or other material likely to contaminate it. If, however, the specimen is more massive, as, for instance, the fractured end of a tensile specimen, it is necessary to do some machining and in such case washing is desirable.

In the authors' procedure washing is carried out in a small Pyrex tube with a sintered crystalline Alundum bottom, the lower part of which is ground into a holder connected through a stopcock to an evacuated filter flask. With the stopcock closed, a small amount of purified acetone is poured over the millings in the tube; the stopcock is then opened and the acetone slowly sucked away. After a minimum of three such washings the sample is placed in a vacuum desiccator and kept overnight at a pressure of about 1 micron (10^{-3} mm. of mercury). In earlier work, ether was used instead of acetone, but its use was discontinued when it was found that in humid weather evaporation of the ether chilled the metal enough to cause an undesirably copious condensation of moisture. The question has also been raised as to whether some trace of acetone may not remain adsorbed or occluded on the sample, but direct comparison of the carbon content of a number of washed samples with that of samples carefully cleaned but not washed indicates that when the washing is properly carried out the acetone remaining is not sufficient to increase significantly the carbon present.

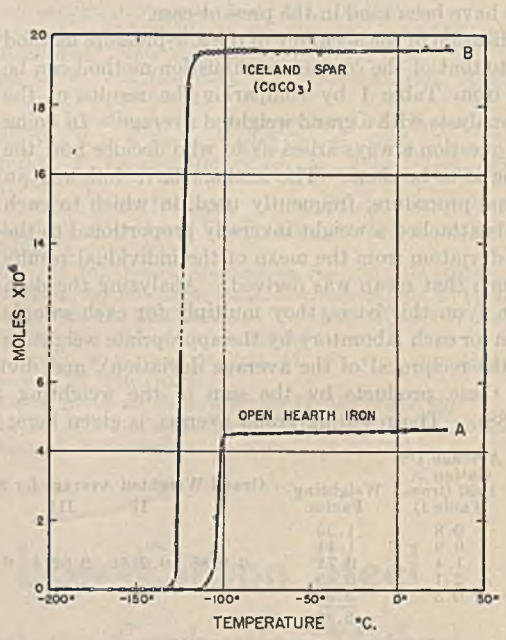

Figure 1. Fractional Vaporization of Condensed Carbon Dioxide

The other question considered is whether the true blank value—that is, with the high crucible temperature resulting from the burning of a sample—is appreciably different from that obtained in the normal way. To gain some information on this point a number of check runs were made on the same material after a preliminary heating of the crucible in oxygen and without opening the system, on the basis that if the higher temperature due to combustion of the sample did cause an increased blank, this blank should decrease on successive combustions, so that the apparent carbon content would successively decrease. The results indicated no significant trend in this direction.

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Photoelectric Photometer—Correction

In the caption of Figure 4 of the article "Photoelectric Photometer for Determining Carbon Disulfide in the Atmosphere" [Ind. Eng. Chem., Anal. Ed., 15, 593 (1943)] the caption should have read: R_6. 250,000 ohms. R_7. 15,000 ohms. R_8. 50,000 ohms.

Shirleigh Silverman

Measurement of Detergency

A Photometer for Determination of Films on Transparent Surfaces

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A simple inexpensive photometer has been designed for the quantitative determination of "hard water" films formed on transparent glass plates during certain detergent processes such as commercial dishwashing. Constructional details and the electrical measuring circuit are discussed and information on the sensitivity of the instrument is presented.

THE calcium and magnesium salts present in hard water react with many detergents to form insoluble compounds. Some of the precipitate thus formed attaches itself to objects being washed and in some processes, such as commercial dishwashing, builds up an unsightly film.

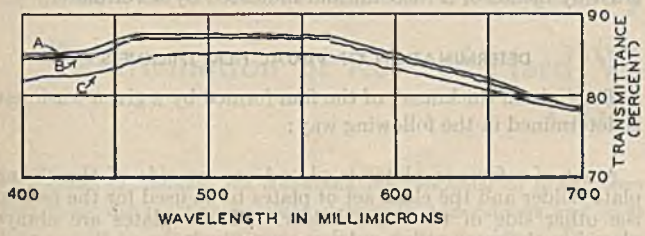

Figure 1. Transmission Data

One would expect the appearance of such film to be a function of such factors as the type of hardness and the amount present in the water used, the type and concentration of detergent used, the nature of the washing, rinsing, and drying processes, the temperature at which the processes are carried out, the nature of the surfaces being washed, the nature of the soil on these surfaces, and finally the number of times the objects are washed.

In commercial dishwashing, as ordinarily practiced, the build-up of unsanitary hard water or so-called lime films has presented a troublesome problem for the operators of public eating places. While progress has been made in recent years in the preparation of detergents which partially overcome this trouble, the relative importance of the various factors involved have not been known quantitatively, nor have satisfactory methods or instruments for use in the study of this problem been established.

This paper describes a photometer which has proved useful in obtaining accurate quantitative information regarding some of the factors involved in a study of this film build-up problem.

A relatively simple method now commonly used permits one to approximate roughly the comparative amounts of film produced when various detergents are used. Drinking glasses, glass plates, or other such objects are washed in a home-type dishwashing machine under known conditions, rinsed, and allowed to air-dry without toweling, and then the objects washed with different detergents are compared visually. Often several cycles of wash, rinse, and air-dry are required before good comparisons can be made. At best, however, such visual comparison yields only semiquantitative information which cannot be reduced to convenient numerical values for future use. An accurate and inexpensive instrument is therefore needed which can replace the visual comparison of objects washed and which will yield numerical and quantitative data. Since these data are indicative of the visual appearance of the film on the washed objects they have, for want of a better term, been designated as values of visual film thickness.

Since it is more difficult to make suitable optical measurements on drinking glasses or other irregularly shaped objects than on flat and regularly shaped ones, squares of plate glass were selected as test plates. Preliminary investigation indicated that the measurement of transmitted rather than reflected light is suitable for the purpose.

In order to determine whether a monochromatic light source would be necessary or of value in such an instrument, several sets of test plates washed with different detergent materials were prepared and the transmission spectra for the films on these plates were studied by means of a General Electric recording spectrophotometer. Transmission data thus obtained for the three most commonly used constituents of alkaline detergents are represented graphically in Figure 1. These studies indicated that the films are all essentially white—i.e., the amount of light transmitted is almost independent of the wave length used and wave lengths between 450 and 600 millimicrons are almost equally well transmitted. The deviations from "whiteness" are essentially independent of the detergent used. Therefore monochromatic light need not be used and any incandescent light source should be suitable with respect to wave length.

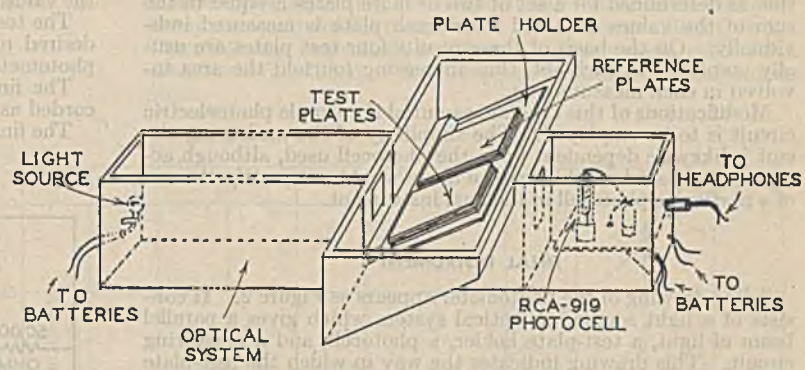

Figure 2. Photometer

An attempt was made to use commercially available photometers, but two construction characteristics rendered them unsuitable for this work. While a small beam of light is advantageous for most analytical work in that it permits the use of small volumes of solutions, it necessitates a large number of measurements if accurate averages are to be obtained on an object covered with an irregular film. Similarly, placing the photocell close to the absorption cell is advantageous in an instrument designed for work associated with colored solutions. For measurement of films on glass plates, however, usefulness is increased by placing the photocell farther from the plates on which measurements are being made. Such construction permits determination of beam transmission rather than diffuse transmission.

MODIFICATIONS IN PHOTOMETER DESIGN

Having selected plate-glass squares 5 inches on a side and 0.125 inch thick as test objects, it was necessary to consider the ways in which these plates could be held in the instrument, so that a large area would be sampled by each measurement. Two methods were considered. The first involved increasing the cross-sectional area of the incident beam of light; the second utilized the principle of tilting the plates at an acute angle with respect to the incident beam. This second alternative was selected in order to avoid the necessity of incorporating in the instrument the more complicated optical system required in utilizing a larger beam of light. This tilting process increased the effectiveness of a given film in reducing the amount of light reaching the photocell.

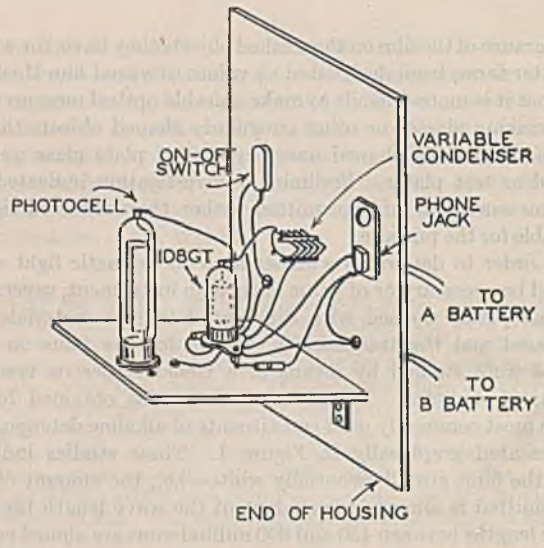

Figure 3. Photometer

The light extinction of a given film was not changed by the simultaneous use of additional plates—that is, the per cent extinction as determined for a set of two or more plates is equal to the sum of the values obtained when each plate is measured individually. On the basis of these results four test plates are usually employed in each set, thus increasing fourfold the area involved in each measurement.

Modifications of this type are essential if a simple photoelectric circuit is to be employed. The simplicity of the measuring circuit is likewise dependent upon the photocell used, although acceptability based on this feature alone would not justify the use of a particular photocell in the final instrument.

FINAL INSTRUMENT

A line drawing of the photometer appears as Figure 2. It consists of a light source, an optical system which gives a parallel beam of light, a test-plate holder, a photocell, and a measuring circuit. This drawing indicates the way in which the test-plate holder, movable perpendicularly to the light beam, is mounted so that either a set of test plates or a set of reference plates may be measured. The standardization of the instrument by means of reference plates is discussed below.

The R.C.A. 919 phototube was selected on the basis of factors previously mentioned. The maximum convenient angle at which the 5-inch test plates could be tilted in a photometer using this photocell was calculated on the basis of the size of the photoactive target and found to be 18°. Using this arrangement it is possible to sample an area of almost 3.5 square inches on each plate with a single transmission measurement, although the phototube has a target area of only 0.9 square inch. Since four glass plates are used simultaneously, a total area of 14 square inches is involved in each measurement.

The plate holder was designed to hold two sets of four plates each. It was constructed in such a way that it compensates for the refraction of the incident beam by the glass plates, so that similar sections of all plates in each set are measured.

For preliminary work the use of excessively expensive equipment was not warranted and hence the photometric circuit best suited to the need was that described by Roberts (*1*). This circuit is of the nature of a relaxation oscillator which causes a series of clicks to be heard in the high-impedance telephone. The frequency of the clicks is, for a given capacity of the condenser, proportional to the intensity of the light falling on the photocell. Light intensity may thus be measured by counting the number of clicks which are heard in a given period of time. A count on clean test plates of 100 clicks per minute has been found convenient. This rate may be attained by adjustment of the variable condenser or of the intensity of the light beam.

When no light falls on the cell, 1 or 2 clicks per minute will occur, owing to electrical leakage across the glass surface of the tubes. This "dark count" is always subtracted from actual counts on plates before the data are recorded or used in further calculations.

The electrical circuit unit of the photometer was mounted as shown in Figure 2, avoiding long lead wires and an extra housing. It is especially important to mount the 1D8GT super control tube in such a way that the light from its filament cannot fall on the phototube. Constructional details are shown in Figure 3; a wiring diagram in Figure 4.

A Mazda lamp Type 82 has served as a convenient light source. In order to ensure a constant intensity of light, energy is supplied from a set of storage batteries which, in turn, are continually fed by a trickle charger. The voltage drop across the lamp is regulated by means of a rheostat and indicated by a voltmeter.

DETERMINATION OF VISUAL FILM THICKNESS

The "visual thickness" of the film formed by a given wash test is determined in the following way:

A set of reference plates is placed on one side of the sliding plate holder and the clean set of plates to be used for the test on the other side of the same holder. (These plates are always placed in the same order and same position.)

The light intensity is adjusted by means of the rheostat to the desired voltage.

The plate holder is moved into position, so that the beam of light passes through the set of reference plates and the number of clicks heard in the headphones in one minute is noted. This value is recorded as R_i.

The plate holder is then moved so that the beam of light passes through the set of plates to be washed and the number of clicks heard in one minute is again counted and recorded as T_i.

The ratio R_i/T_i is calculated. Since it is constant for a given set of test plates when compared to a given set of reference plates, the value is indicated by K.

The test plates are washed, rinsed, and dried according to the desired procedure and returned to their former position in the photometer.

The final reference-plates count is again determined and recorded as R_f.

The final test-plates count is determined and recorded as T_f.

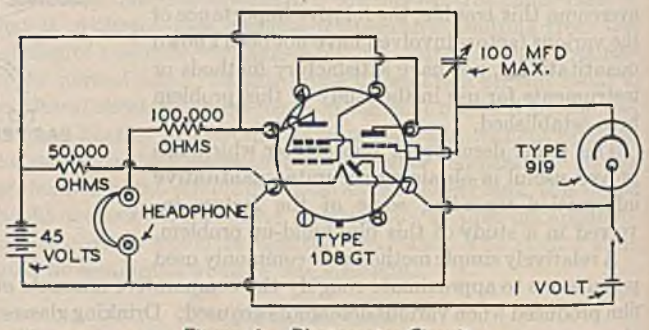

Figure 4. Photometer Circuit

The final transmission of the test plates as compared to their initial transmission is given by the formula:

$$\frac{R_i}{T_i} \times \frac{T_f}{R_f} \times 100 = K\frac{T_f}{R_f} \times 100 = \text{apparent \% transmission}$$

When $R_i = R_f$—that is, when the photometer has remained in a stable condition—this equation becomes:

$$\frac{T_f}{T_i} \times 100 = \text{apparent \% transmission}$$

The "visual thickness" of the film on the test plates is then calculated by use of the formula:

Visual thickness of film = apparent % extinction = 100% − apparent % transmission

The washing and measuring procedure is then repeated the desired number of times. For convenience each repetition of this procedure is called a wash cycle.

REPRODUCIBILITY OF MEASUREMENTS

The reproducibility of measurements was determined by selecting a set of test plates which, after washing, had an apparent transmission of 57.0%. Over a period of 2 days this set of plates was measured ten times. After each measurement the plates were removed from the photometer and placed in a tightly covered wooden box. The "reference-plates count" was intentionally varied from 78 to 100 clicks per minute. The probable error was then calculated and found to be ±0.52% for a single reading or ±0.17% for the average of 10 readings.

Experience has shown that the errors resulting from the photometer are negligible as compared to those arising from variations in the wash procedure.

CONCLUSION

The photometer described is easily and cheaply constructed and possesses sufficient sensitivity to permit its use in the development of performance tests for certain types of detergents.

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PRESENTED in part before the Division of Industrial and Engineering Chemistry at the 104th Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y.

(Measurement of Detergency. . .)

Determination of Rate of Hard Water Film Formation in the Washing of Glass Objects

A method is outlined for measuring the tendency of precipitates formed by the reaction between detergents and calcium and magnesium salts to adhere to glass surfaces during washing. Data are presented to show the reproducibility of results obtained by the suggested method and the ease and accuracy with which differences between detergents may be determined.

THE relatively recent introduction of "polyphosphates" (*1–4*) has given the detergent chemist convenient materials with which to decrease the rate at which film will appear on dishes and glassware when normal washing conditions are employed. However, there has been no satisfactory method of quantitatively measuring this rate of film formation.

This paper reports a test capable of yielding reproducible results quantitatively evaluated by means of the photometer described in the previous paper (*5*).

METHOD

WASHING MACHINE. A home-type General Electric dishwashing machine has been found applicable to this type of test. Basically it consists of a covered tank, at the bottom of which is located a small impeller-type agitator. This agitator revolving at a speed of approximately 1700 r.p.m. throws the wash (or rinse) solution in the form of a fine spray over the test objects which rest on a wire rack in the upper portion of the machine.

TEST OBJECTS. Pieces of plate glass 5 inches square and 0.125 inch thick cut from a single sheet of glass have been used as test objects. It is possible that the film build-up may be different on different types of glass and may vary with the physical as well as chemical nature of the surfaces of the test objects. Because the initial purpose of this work was to study the relative effects of different detergents rather than of different surfaces, these test objects were considered appropriate.

PREPARATION OF STANDARD HARD WATER. Water of known hardness may be obtained by drawing from some natural source enough water for the tests to be performed and then determining its calcium and magnesium content by analytical methods. A somewhat simpler method consists of softening a natural supply of water by means of a zeolite softener and then increasing its hardness by the addition of concentrated solutions of calcium and magnesium salts. For this purpose the authors have used calcium chloride and magnesium sulfate; care must be take in adding these salts to prevent the precipitation of calcium sulfate.

ADDITION OF DETERGENT. The desired weight of detergent for each cycle may be added directly to the wash water in the machine. Since the volume of wash water is small and the concentration of detergent is usually low, relatively small amounts of detergent are added at one time. Under these conditions a serious error may result, in that the composition of all additions may not be representative of the composition of the detergent being tested. This error may be partially nullified by adding a given volume of a concentrated solution of the detergent by means of an automatic pipet.

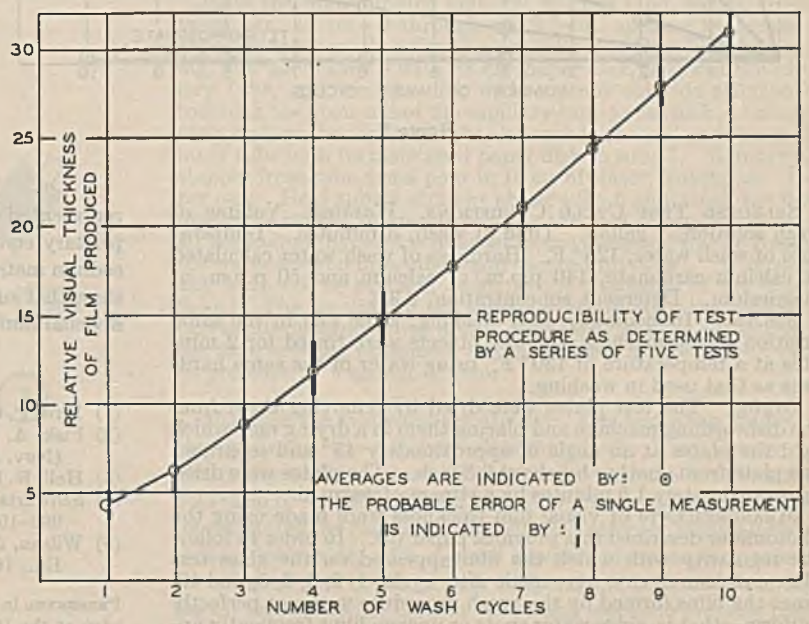

Figure 1

Table I. Reproducibility

(Detergent, trisodium phosphate. Concentration, 0.32%. Water hardness, Ca = 140 p.p.m., Mg = 50 p.p.m.)

Cycle	Apparent % Extinction 1	2	3	4	5	Av.	Probable Errors (in Terms of Apparent % Extinction) r	R
1	3	4	5	5	5	4.4	0.56	0.25
2	6	8	5	6	8	6.2	1.20	0.54
3	10	9	7	9	10	9.0	0.82	0.37
4	13	10	10	12	15	12.0	1.42	0.63
5	16	16	12	13	18	15.0	1.60	0.72
6	20	19	16	16	19	18.0	1.26	0.56
7	23	22	20	20	22	21.4	0.82	0.37
8	25	25	22	24	27	24.6	1.22	0.54
9	29	31	26	27	28	28.2	1.35	0.60
10	31	32	29	31	33	31.2	0.95	0.42

Zeolite-softened water is heated to 160° F. by means of a thermostatically controlled water heater. A gallon of this water is drawn from the heater, hardened as previously described, and then poured into the machine. The temperature in the machine is indicated by a mercury-actuated dial-type thermometer whose bulb extends downward from the top of the machine. On starting the spray action the thermometer reading increases rapidly, until after about 15 seconds a maximum is reached and is recorded as wash temperature or rinse temperature. No decrease in temperatures has ever been noted during the 3-minute wash period.

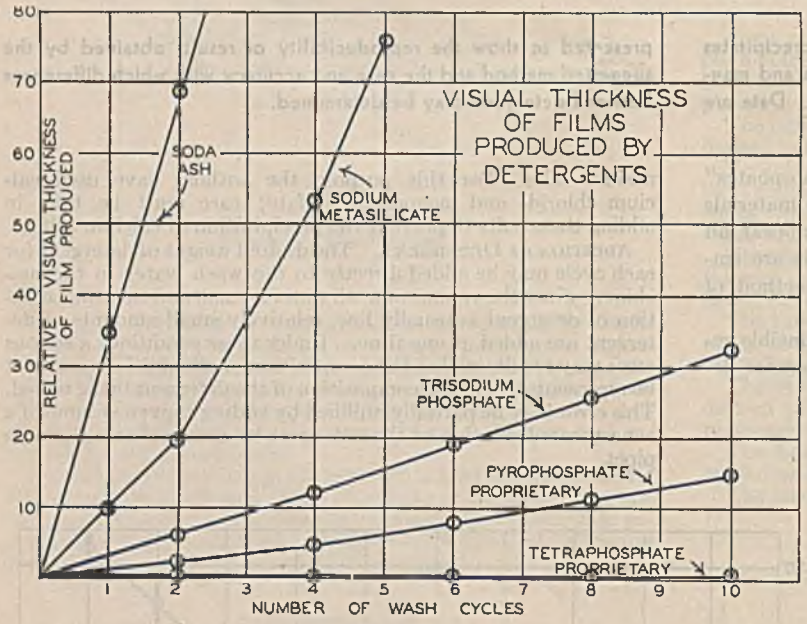

Figure 2

Selected Test Cycle Conditions. *Washing.* Volume of wash solution, 1 gallon. Time of wash, 3 minutes. Temperature of wash water, 125° F. Hardness of wash water calculated as calcium carbonate, 140 p.p.m. of calcium and 50 p.p.m. of magnesium. Detergent concentration, 0.3%.

Rinsing. Immediately after washing, while still in the same position in the machine, the test objects were rinsed for 2 minutes at a temperature of 130° F., using water of the same hardness as that used in washing.

Drying. The test plates were dried by removing them from the dishwashing machine and placing them in a drying rack which held the plates at an angle of approximately 45° and separated one plate from another by about 0.5 inch. The plates were dried in approximately 1.5 minutes by a stream of warm air.

Measurements of visual film thickness were made using the photometer described in a previous paper (*5*). In order to follow the regularity with which the film appeared on the glass test plates, measurements were made after cycles 1, 2, 4, 6, 8, and 10. Since the films formed by this wash procedure were not perfectly uniform—that is, since water spots or uneven films frequently appeared on the plates—measurements were made on two areas of each test plate. This represented a measurement on 28 square inches of plate area. The instrument was standardized by making a measurement on the set of reference plates both before and after the measurements were made on the set of test plates.

REPRODUCIBILITY OF RESULTS

The reproducibility of the results obtained by this test procedure is indicated by Table I. These data were obtained by repeating tests in which all controllable variables were maintained as nearly constant as was experimentally possible and using the conditions outlined above.

The average probable error for a single reading was approximately 1.0% extinction. The significance of this probable error is best understood after studying Figure 1, in which visual film thickness has been plotted against the number of times the test plates were washed, rinsed, and dried. Because of the reproducibility of this type of test, differentiation between detergents which give nearly similar results is possible.

DATA

Film build-up curves for three common constituents of commercial dishwashing compounds are shown in Figure 2. All data resulted from tests utilizing the conditions outlined above, the only variable being the composition of the detergent used.

Of the three alkaline materials most commonly found in commercial dishwashing detergents, commercial trisodium phosphate, $Na_3PO_4.12H_2O$, produced the least film during ten repeated washing cycles. Sodium metasilicate, $Na_2SiO_3.5H_2O$, produced a heavier film than the trisodium phosphate under the test conditions but less film than soda ash, Na_2CO_3.

The use of certain molecularly dehydrated phosphates in reducing hard water film formation is illustrated by the two remaining curves. A notable improvement may be obtained by the introduction of tetrasodium pyrophosphate into the detergent. A proprietary containing 25% tetrasodium pyrophosphate, 40% sodium metasilicate, and 35% soda ash produced after 10 cycles a film having a relative visual thickness of only 15 units as compared to a thickness of 31 units produced by trisodium phosphate alone.

Greater effectiveness in preventing hard water films is possessed by other phosphates commonly referred to as polyphosphates. One of these, commercially designated as sodium tetraphosphate, $Na_6P_4O_{13}$, was selected for testing. Chemical analysis of this glassy material indicated a composition which may be represented by $3Na_2O.2P_2O_5$. The results obtained with a proprietary containing 32% of this sodium tetraphosphate, 40% of sodium metasilicate pentahydrate, and 28% of sodium carbonate show that such a detergent, under identical test conditions, yields a visual film thickness of less than 2 units.

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Presented in part before the Division of Industrial and Engineering Chemistry at the 104th Meeting of the American Chemical Society, Buffalo, N. Y.

A Compact Field Apparatus for Determination of Lewisite or Mustard Gas

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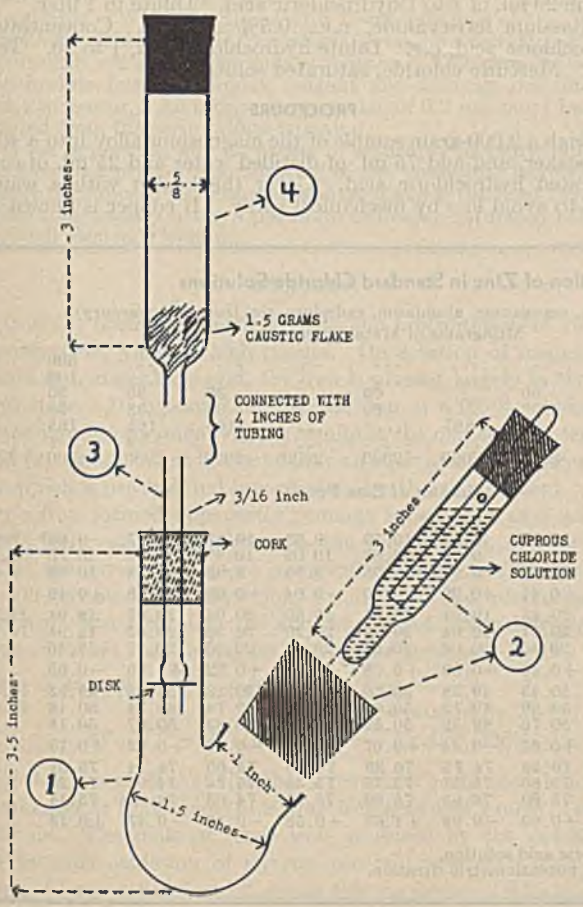
MEMBERS of the West Orange, N. J., Gas Officers' Defense Staff have developed a compact apparatus for field detection of lewisite or mustard gas (liquid). Its simplicity makes it adaptable also for laboratory use.

When liquid lewisite is treated with 15% sodium hydroxide solution, acetylene is liberated and is detected in this apparatus by the formation of deep red cuprous acetylide on a disk of filter paper, freshly moistened with cuprous chloride solution. If the cuprous chloride solution is practically colorless, the moistened disk turns pink, then gradually deep red if considerable acetylene is generated; if the cuprous chloride solution is blue, the disk turns purplish red and the color gradually deepens. The reaction is distinctive, sensitive, and quantitative.

To test for liquid mustard, the paper disk is moistened with sodium platinic iodide–starch solution, without addition of sodium hydroxide or other reagent. In the presence of mustard the color changes from violet to strong blue. Gentle heat hastens the reaction.

APPARATUS

The main tube, 1, has an expanded bottom bulb 3.75 cm. (1.5 inches) in diameter, on the side of which is blown a 2.5-cm. (1-inch) opening. A rubber stopper, 2, fits tightly in this opening and is provided with a 0.6-cm. (0.25-inch) hole in which is pushed tightly the end of a small vial containing the cuprous chloride reagent used to moisten the disk just prior to making the test for lewisite. A rubber stopper is very satisfactory here, as neither lewisite nor mustard has any immediate effect upon it. After the test has been completed, the entire apparatus is taken apart and thoroughly scrubbed with calcium hypochlorite sludge.



Inner tube 3, centrally located in the upper part of tube 1, is supported in a cork having a small V cut out along its entire length, so that when cork and tube are in position, the gas evolved will vent through this cork and prevent the building up of pressure during the test. A slight bulb or bulge is blown 1.25 cm. (0.5 inch) from the lower extremity of this inner tube. Tube 4, connected with the upper end of tube 3 by 10 cm. (4 inches) of rubber tubing, has a capacity of 15 cc. Tube 4 has 1.5 grams of flake sodium hydroxide placed in it and is then tightly stoppered. Its contents will remain in perfect condition for any length of time. A small glass bead fits into the rubber tube, connecting tube 4 with the upper end of tube 3, about 2.5 cm. above the point where the rubber tube is fastened to tube 3. This bead, or valve, prevents liquid from entering tube 1. When the test is to be made, the side of the bead is pinched with the thumb and forefinger, causing a channel to be formed through which the caustic solution flows into tube 3, then into tube 1.

The filter paper disk upon which the color reactions are produced is cut to a diameter slightly smaller than that of the upper part of tube 1. In its center is cut a small hole of a size which will allow the disk to be pushed on the lower end of tube 3 up to the point where it meets the bulge. A small rubber band is twisted around the tube, flush with the underside of the paper disk, to keep it in position.

The supporting stand may consist of nothing more than a square block of wood containing a slight hollow in the center to support the bottom of tube 1 and an upright piece of wood with a clip near the top to support the upper end of the tube.

CONSTRUCTION OF VIAL AND CAPILLARY TUBE. The vial is made from soft-glass tubing of about 1.25-cm. (0.5-inch) diameter, the lower end being drawn down to fit the 0.6-cm. (0.25-inch) hole in the rubber stopper and sealed. The total length of the vial is 7.5 cm. (3 inches). The capillary tube, which acts as a dropper tube, inside the vial is 3-mm. glass tubing, open at the lower immersed end and having a very small hole blown in it just below the point where the lower end of the rubber stopper, which closes the vial, is located. The upper end of the capillary tube is sealed.

PROCEDURE

Place the contaminated material, such as sand, leaves, rubble, twigs, etc., in tube 1 through the 2.5-cm. opening by means of tweezers or tongs, then firmly place rubber stopper 2 in this opening. Remove tube 3 with its dry paper disk, take out the capillary tube, and wet the disk with cuprous chloride solution by touching the open end of the capillary tube to the disk. Immediately replace the capillary tube and cork in the vial and return the inner tube with its moistened paper disk to tube 1. Remove the stopper from tube 4 and pour in 10 cc. of water, leaving the stopper out. Hold tube 4 straight above tube 3 and pinch the bead inside the rubber tubing, regulating the flow of solution, so that all the sodium hydroxide flake will have dissolved by the time all the water has run into tube 3 and thence into tube 1. (Considerable heat will be evolved, owing to the dissolving of the caustic flake.) The reaction of the caustic solution upon the lewisite is practically instantaneous and if any such "gas" is contained in the sample being examined, the filter paper disk will soon show its presence by a change of color.

Although the minimum sensitivity of this test when applied in the apparatus has not been determined, the West Orange gas laboratory staff has obtained very positive results with less than 0.25 drop of lewisite. The presence of arsenic may be confirmed by extracting the contaminated material, after the treatment with sodium hydroxide, with a small amount of water, neutralizing the solution thus obtained with 50% sulfuric acid, and then testing for arsenic by the Gutzeit test, using mercuric bromide paper and not mercuric chloride paper for the arsine color reaction.

ADVANTAGES OF APPARATUS

The chamber in which the acetylene or mustard vapors are brought into contact with the moistened reactor paper is very small, thus concentrating the amount of reactive gases in contact with the reagent.

The use of dry sodium hydroxide flake in tube 4 prevents deterioration and spilling of alkali.

The addition of the water to the dry sodium hydroxide just before use produces considerable heat, speeding the reaction. In the case of lewisite, this decreases the solubility of the acetylene in the liquid reactive mass and thereby increases to a maximum the amount of acetylene generated.

The filter paper disk, of practically the same area as the chamber through which the reactive vapors must pass, gives quicker and better contact with such vapors than a paper strip suspended within the reaction chamber. The disk is placed at a point where contamination with the caustic solution is impossible.

The rounded bottom of tube 1 is an advantage if one desires to heat the contaminated material gently (in case of mustard gas) for more rapid volatilization of the vapors.

Placing the cuprous chloride solution in the small vial, which in turn is carried at all times in the rubber stopper, eliminates the necessity of carrying a separate bottle for this reagent.

The entire apparatus may conveniently be carried in a coat pocket or field kit.

Routine Determination of Zinc in Magnesium Alloys

A Volumetric Method

LLOYD GEORGE MILLER, ALBERT J. BOYLE[1], AND ROBERT B. NEILL
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A rapid accurate volumetric method for the determination of zinc in magnesium alloys involves the precipitation of zinc in 1 *N* hydrochloric acid with excess standard potassium ferrocyanide. The excess is subsequently determined by titration with standard ceric sulfate solution. Manganese, cadmium, tin, and small amounts of iron do not interfere. The method is capable of an accuracy ranging from 1 to 5% of the amount of zinc present in magnesium-base alloys of high and low zinc content, respectively.

IN VIEW of the large number of magnesium-base alloys containing zinc, the determination of this element has become increasingly important to the magnesium industry. The Lang method (*4*) modified by Casto and Boyle (*1*) requires the elimination of manganese, cadmium, tin, and copper from the sample, and is limited largely to magnesium-base alloys containing aluminum and manganese. If the zinc content of the magnesium alloy is less than 1% a preliminary separation with hydrogen sulfide becomes necessary.

The method described in this paper is applicable to magnesium-base alloys containing from 0.05 to several per cent zinc, and is recommended for routine analytical control. Cadmium, tin, and manganese offer little interference. The error due to iron is largely compensated by a step in the procedure employing the use of potassium ferricyanide. If copper is present, it is removed with test lead.

REAGENTS

POTASSIUM FERROCYANIDE, 0.025 *N* solution. Dissolve 11.2 grams of potassium ferrocyanide trihydrate analytical reagent grade, in 1 liter of distilled water containing 0.2 gram of sodium carbonate. Let the solution stand overnight, filter, and standardize against zinc chloride solution.

CERIC AMMONIUM SULFATE, 0.025 *N* solution (*5*). Dissolve 22 grams of ceric ammonium sulfate dihydrate in 1 liter of distilled water containing 28 ml. of concentrated sulfuric acid. The solution is approximately 0.025 *N*. Filter the solution, and adjust the volume so that 1 ml. of solution is equivalent to 1 ml. of standard potassium ferrocyanide solution.

TRI-*o*-PHENANTHROLINE FERROUS SULFATE [$(C_{12}H_8N_2.H_2O)_3$-$FeSO_4$] solution. Dissolve 1.485 grams of *o*-phenanthroline ($C_{12}H_8N_2.H_2O$) in 100 ml. of 0.025 *M* aqueous solution of ferrous sulfate.

STANDARD ZINC SOLUTION. Dissolve 1 gram of zinc metal, C.P., in 20 ml. of 1 to 1 hydrochloric acid. Dilute to 1 liter.

Potassium ferricyanide, C.P., 0.5% solution. Concentrated hydrochloric acid, C.P. Dilute hydrochloric acid, 1 to 10. Test lead. Mercuric chloride, saturated solution.

PROCEDURE

Weigh a 2.000-gram sample of the magnesium alloy into a 400-ml. beaker, and add 75 ml. of distilled water and 25 ml. of concentrated hydrochloric acid. Cover the beaker with a watch glass to avoid loss by mechanical spray. If copper is known to

Table I. Estimation of Zinc in Standard Chloride Solutions

(In the presence of magnesium, manganese, aluminum, cadmium, tin, iron, and mercury)

	Milligrams of Metal Present[a]										
Mercury	...	...	...	...	...	...	...	...	500	...
Tin	...	...	...	...	...	...	...	...	100	...
Manganese	...	30	60	...	60	...	30	30	30	...
Cadmium	...	...	...	...	60	60	38	38	38	...
Aluminum	...	...	...	165	...	...	165	165	165	...
Iron	...	...	...	...	...	...	1	2	1	1
Magnesium	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
Zinc Taken	Milligrams of Zinc Found										
Mg.											
10	9.70	9.52	9.83	10.37	9.57	10.70	9.83	10.01	9.57	9.86[b]	9.65
10	9.55	9.88	10.01	10.42	9.60	10.83	10.09	10.29	9.52	10.75	9.70
10	9.91	9.80	9.98	10.44	9.96	10.55	9.96	9.93	9.78	10.62	9.45
Av. error	−0.28	−0.27	−0.06	+0.41	−0.29	+0.69	−0.04	+0.08	−0.38	+0.40	...
20	19.94	19.74	20.02	20.43	19.94	20.76	20.30	20.04	20.07	18.94	19.76
20	20.04	20.15	20.17	20.51	20.04	20.68	20.20	20.30	20.02	18.94	19.87
20	19.76	20.02	20.04	20.45	20.02	20.61	20.04	20.33	20.17	19.46	...
Av. error	−0.09	−0.03	+0.08	+0.46	±0.00	+0.68	+0.18	+0.22	+0.09	−0.65	...
50	50.00	49.64	50.25	50.43	49.38	50.76	50.23	50.18	50.12	49.92	49.87
50	49.82	49.69	50.48	50.66	49.72	50.66	49.56	49.74	49.74	50.18	49.48
50	49.84	49.79	50.15	50.76	49.59	50.59	50.12	49.82	50.07	50.18	...
Av. error	−0.11	−0.29	+0.24	+0.61	−0.44	+0.67	−0.03	−0.09	−0.02	+0.13	...
75	75.37	75.29	75.44	76.26	74.75	76.39	75.55	74.60	74.14	75.01	...
75	74.83	75.26	75.37	75.80	75.32	75.75	75.44	75.24	74.93	75.26	...
75	75.03	74.29	75.60	75.90	74.65	75.96	75.75	74.65	74.83	75.14	...
Av. error	+0.08	−0.03	+0.47	+0.69	−0.09	+1.03	+0.58	−0.19	−0.37	+0.13	...

[a] All determinations made in hydrochloric acid solution.
[b] Results in this column determined by potentiometric titration.

[1] Present address, College of Medicine, Wayne University, Detroit 26, Mich.

Table II. Zinc Ferrocyanide Precipitates for Manganese Contamination[a]

Manganese Added	Manganese Found in Precipitate	Zinc Added	Zinc Found	Zinc Error (Determined)
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
10	0.30	10	10.20	+0.20
30	0.58	10	10.60	+0.60
60	0.78	10	10.60	+0.60
10	0.30	20	20.60	+0.60
30	0.54	20	20.58	+0.58
60	0.78	20	20.60	+0.60
10	0.16	30	30.43	+0.43
30	0.60	30	30.78	+0.78
60	0.68	30	30.50	+0.50
10	0.30	40	40.80	+0.80
30	0.52	40	40.98	+0.98
60	0.68	40	41.00	+1.00

[a] Each determination made in presence of 2 grams of magnesium metal as chloride.

Table III. Estimation of Very Low Zinc Content in Magnesium Alloy

Polarographic	Proposed Method
%	%
0.065	0.07
0.067	0.07
0.065	0.07
0.065	0.07
0.095	0.10

be present in the alloy, add approximately 3 grams of test lead to the sample, and boil for 5 minutes. Decant the solution through a Whatman No. 1 filter paper into a 600-ml. beaker, wash the residue three times with 10-ml. portions of distilled water, cool to approximately 45° C., and add 2 ml. of potassium ferricyanide reagent. Add a measured excess of standard potassium ferrocyanide reagent dropwise with rapid mechanical stirring. The dropwise technique should be observed for the first few milliliters, after which the reagent may be added more rapidly. Allow the precipitate to stand for 5 minutes, and filter by suction through a 9-cm. Büchner funnel into a 500-ml. suction flask. The filter pad consists of a No. 42 Whatman paper covered with a thin layer of asbestos. Wash two times with 15-ml. portions of 1 to 10 hydrochloric acid. Titrate the excess potassium ferrocyanide reagent with standard ceric sulfate solution. Two drops of *o*-phenanthroline ferrous complex reagent are used as the internal redox indicator. An indicator correction of 0.2 ml. must be subtracted from the ceric sulfate titration.

If tin is present, add an excess of saturated mercuric chloride solution just prior to the addition of the potassium ferricyanide reagent. Proceed as described above, making the final titration potentiometrically using a platinum indicator–saturated calomel half-cell electrode system.

DISCUSSION

Iron (*3*) normally interferes with the precipitation of zinc as ferrocyanide, yielding high results. On solution of magnesium alloys in hydrochloric acid, the iron is present largely in the ferrous state. It appears that the addition of a 0.5% solution of potassium ferricyanide reagent results in the oxidation of ferrous iron (*2*), producing at the same time an equivalent of ferrocyanide ion which is precipitated immediately by the zinc present. The ferric iron formed apparently remains in solution as a soluble ferric ferricyanide complex. As the precipitation of zinc proceeds, the ferric iron present is precipitated as ferric ferrocyanide. It will be noted from Equations 1 and 2 that more ferrocyanide ion is produced through the addition of potassium ferricyanide than can react stoichiometrically with the ferric iron formed:

$$Fe^{++} + Fe(CN)_6^{----} = Fe^{+++} + Fe(CN)_6^{----} \quad \text{(precipitated by } Zn^{++}) \quad (1)$$

$$4Fe^{+++} + 3Fe(CN)_6^{----} = Fe_4[Fe(CN)_6]_3 \quad (2)$$

If it is assumed that the above reactions go to completion, it would appear that 1 mole of ferrous iron produces 1 mole of ferrocyanide. The mole of ferric iron produced by the potassium ferricyanide oxidation of ferrous iron will now react with 0.75 mole of ferrocyanide, which means that an excess of 0.25 mole of ferrocyanide is produced. This yields low results for zinc, as illustrated in Table I. The iron normally encountered is much less than that added in this study. If care is not exercised in the filtration of a sample containing very low zinc and a few hundredths of a per cent of iron, a small quantity of colloidal Prussian or Turnbull's blue formed in the presence of excess potassium ferrocyanide may pass through the filter. This yields low results for zinc. The dropwise addition of standard ferrocyanide tends to reduce this potential error.

The acid concentration employed in this procedure is sufficiently high to avoid quantitative interference of such elements as cadmium, manganese, or tin. Cadmium alone does not particularly interfere. Cadmium and manganese together (or manganese alone) produce a slight deviation from true values. It will be noted from Table I that manganese causes high results. Table II illustrates the amount of manganese in a number of zinc ferrocyanide precipitates. The interference of stannous tin is overcome by addition of an excess of mercuric chloride prior to addition of potassium ferricyanide reagent. Under these conditions, the end point with the redox indicator is indistinct; therefore, the titration must be carried out potentiometrically. Ammonium salts, excess sulfates, and nitrates interfere.

A single analysis on a magnesium alloy may be completed in 30 minutes. The method is capable of an accuracy ranging from 1 to 6% of the amount of zinc present on high and low magnesium-zinc alloys, respectively. On magnesium alloys containing less than 0.1% zinc the method is much less accurate (Table III).

In general, the method compares favorably with the accuracy attained by the hydrogen sulfide procedure for zinc and, in the hands of the average analyst, gives greater precision. Table IV illustrates the agreement between the two methods.

Segregation of zinc in magnesium alloys may account for some of the differences. Determinations were not made on aliquots. Therefore, Table IV shows the agreement in results which may be expected in ordinary routine analysis by the separate procedures.

Table IV. Estimation of Zinc in Magnesium Alloys

Hydrogen Sulfide Procedure	Proposed Procedure	Difference Based on Hydrogen Sulfide Method
%	%	%
0.36	0.36	±0.00
0.21	0.20	−0.01
0.36	0.37	+0.01
0.18	0.18	±0.00
0.20	0.21	+0.01
0.52	0.51	−0.01
0.37	0.40	+0.03
0.42	0.43	+0.01
0.43	0.43	±0.00
0.48	0.48	±0.00
1.13	1.14	+0.01
3.09	3.15	+0.06
3.09	3.13	+0.04
3.14	3.14	±0.00
3.19	3.18	+0.01
3.24	3.26	+0.02
3.10	3.16	+0.06
3.14	3.17	+0.03
3.29	3.33	+0.04
3.04	3.10	+0.06

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MICROCHEMICAL BALANCES

Errors of the Kuhlmann Balance

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Methods are described for the location of many of the errors found in microchemical balances, particularly in the Kuhlmann balance. These fall into two general groups, those varying with the environment and those entirely resident in the instrument. In the first group are errors due to temperature gradients in the balance case, to humidity changes, to uniform temperature changes, and to magnetic influences. In the second group are those due to reading, to the imperfection of the knives, to poor arrestment design, to poor rider design, and to imperfect machining of the rider notches. Errors varying with environment can be controlled by the manufacturer by redesigning the instrument or by the user by controling the environment. Under unfavorable conditions, they may range up to several hundred micrograms but under usual weighing conditions they are in the range of 0 to 20 micrograms. Random errors in the instrument are found to have a standard deviation of nearly 5 micrograms at full load. Methods are described for reducing the order of magnitude of these errors to about one microgram. Later communications will deal with other errors to be found in other balances and with details of design and construction which will eliminate these errors.

IT IS now generally recognized that with respect to speed and economy the methods of milligram analysis are superior to those of decigram analysis which have long been standard in organic analytical work. It is not so generally recognized that milligram methods as presently practiced are almost uniformly inferior in accuracy to the best decigram procedures which they are designed to replace. The accuracy of the determination of carbon and hydrogen on the milligram scale has been reported upon by Power (*27*). His findings contrast with the accuracy reported in decigram analyses by Benedict (*2*), Morse and Taylor (*25*), Barnett and Thorne (*1*), Bruun (*3*), Coffari (*4*), and Wing (*39*), to select only a few examples. In 1933 a program of research was initiated in this laboratory which aimed at discovering the fundamental reasons for the discrepancy in accuracy between milligram and decigram methods.

It was soon discovered that weighing is one of the most important sources of error in the milligram analysis for carbon and hydrogen. This alone is larger than the total error of most of the decigram methods referred to above. This finding has been substantiated by Corner and Hunter (*6*) and the Committee on Microchemical Balances of the American Chemical Society (*32*). When using milligram methods, the chemist is no longer secure in his accustomed assumption that the accuracy of his weighings is greater than the accuracy of his other manipulations. As a result of this finding, a systematic investigation to determine the causes of the irregularities observed was begun in this laboratory. This paper shows the presence and causes of weighing errors sufficient to bring about a maximum analytical error of 0.3% in carbon, assuming a 3-mg. sample containing 50% carbon with ideal laboratory conditions. With disturbing environmental conditions, this error may mount to 0.6% or even higher. Under normal conditions, the error would not frequently reach the maximum value.

Because the Kuhlmann balance is the most widely used among analysts, its performance was investigated first. In view of reports on the performance of the Kuhlmann balance in the literature and the results reported in this paper, it is amazing to find the statement by Pregl-Roth (*28*) that "this balance (the Kuhlmann) represents the limit of possible achievement in the construction of balances of precision". It seems certain that the authors, in this instance, succumb to a common failing in confusing sensitivity with accuracy in balances. Thus they say, "it appears to be easily possible to obtain, with this instrument, an accuracy of ±0.001 mg. on a weight of 20 mg.—that is, a sensitiveness of 10^{-7}". The author has examined sixteen Kuhlmann balances in several laboratories and in no case was half an hour's examination required to show that the accuracy of each instrument was only a fraction of its sensitivity. The studies recorded in this paper show that any analyst can make changes which will improve the accuracy of his balance.

This communication presents test methods for locating and evaluating the errors of the Kuhlmann balance, many of which are also present on most other balances, and gives suggestions which will enable the owner of a balance to decrease the magnitude of many of the errors. Later papers in the series will attempt to assay all the features of design and workmanship in balances which can cause errors as large as 1 microgram.

In the course of these studies it was realized that no palliative measures would be sufficient to overcome the fundamental weaknesses in design of the Kuhlmann balance and that the only solution to the analyst's problem would be the construction of an entirely new balance with the errors of earlier designs eliminated. In the last few years, the importance of a domestic source of supply has become evident to all and this series of papers will present the results of numerous experiments on balance design, new and improved test methods, details of construction, tolerances, and specifications, which will permit domestic manufacturers to produce instruments superior to the best foreign instruments and with a reproducibility of 1 microgram under laboratory conditions. As a result of this study a new balance has been constructed in the author's laboratory which gives microgram accuracy. Details of its construction will be given in the appropriate places in the series.

Examination of the data shows that the errors found may be divided into two categories: (1) errors caused by environmental changes and (2) errors entirely resident in the instrument. This fact has given rise to some confusion in specification and to variations in reports on balance performance.

Errors Caused by Environmental Changes

Manufacturers possessing air-conditioned testing rooms with stable supports are frequently able to obtain better results with their instruments than users with laboratories less favorably equipped. Makers who are unable to guarantee that their instruments are so constructed as to be free from errors due to atmospheric and similar changes should know the magnitude of the effects to be expected and should be able to instruct prospective purchasers as to the best precautions to be taken under the available laboratory conditions. Their final objective should be to produce instruments which are not affected by the environmental changes encountered in a chemical balance room without air-conditioning or other special preparation.

Environmental changes which may affect balances and weighings are changes in temperature, humidity, barometric pressure, magnetic field, tilt of the building and balance supports, and vibration.

ERROR DUE TO TEMPERATURE GRADIENT

Manley (*19*) demonstrated with a differential bolometer that temperature differences exist within a balance case under the conditions of ordinary use and showed how the beam of the

balance could be protected against such an effect. In a later article (*24*) he ascribed zero point shifts to lengthening of the beam due to heating and to the change in buoyancy of air. Both effects should cause the pointer to shift as if the heated side of the beam were more heavily weighted.

In the summer of 1935 F. S. Arguelles of Seederer-Kohlbusch, Inc., called the author's attention to the fact that this could not be the true explanation, since it is easily demonstrated that the pointer actually shifts as if the heated side of the beam were less heavily weighted. This can be illustrated readily even with a relatively insensitive balance by placing a hot object above one of the pans. A rising current of air will result, which will cause an immediate illusory decrease in weight on the heated side. As far as the author is aware, no experimental method has been proposed heretofore for demonstrating whether or not the beam lengthens as Manley suggested (*26*). The results of such an experiment are reported here.

A study was made of the shift of the balance rest point under temperature differentials, with and without load. If the conditions causing motion of the air near the beam are reproduced, the apparent decrease in weight due to a rising air current will be the same at all loads. On the other hand, any effect due to an increase in the length of the beam will cause an apparent increase in weight proportional to the load transported away from the center knife by the elongation of the beam. By varying the weight on the end knife, the effect due to the elongation of the beam may be differentiated from that due to the direct action of air currents. The experimental method by which this differentiation is accomplished is given below.

Experiments. The following experiments cannot be performed with a Kuhlmann balance because of the impossibility of reducing sufficiently the initial temperature differential in the Kuhlmann case. Instead, it is necessary to use a special experimental balance, heat-insulated to eliminate temperature gradients. The insulation process will be described in detail in a later communication.

A wire stand is arranged inside the balance case to support a heated object—for example, an empty absorption tube—in approximately the position which it would occupy if it were being weighed but so that no contact is actually made with the moving parts of the balance. Any weight desired may then be placed upon the pans, the heated object inserted, and the excursion of the pointer noted at various times. The differences between the readings when loaded and those when unloaded at corresponding times, all other factors remaining constant, permit calculation of the effect due to changes in arm length of the beam. The absorption tube is placed in a 500-cc. glass cylinder in an air thermostat heated 5° to 10° C. above room temperature and allowed to remain until equilibrium has been established. It is then transferred inside the cylinder to the balance case and placed upon the wire stand as quickly as possible and the time is noted, preferably with a stop watch. Using this technique, satisfactory results may be obtained in plots of the displacement of the balance against the time elapsed after inserting the warmed tube.

The experiment is performed first with unloaded pans and then with a 20-gram load. The two runs are plotted, the weight of the pans and stirrups is determined, and a third curve is constructed which represents an extrapolation to zero load at the end knife. When the beam expands, it transports a portion of its own weight which cannot be calculated without knowing the temperature gradient in the beam from the center knife to the end knife. The major portion of the load which it transports is upon the end knife, however, and for this reason we have chosen to neglect the weight of the expanding portion of the beam. With this inaccuracy, the extrapolated curve represents the effect due to the direct action of the air stream alone, the difference between this and the actual curves being due to the expansion of the beam when heated by the air stream. For a further control, a thermocouple may be installed in the case with one junction as near as possible to the heated end of the beam and the other at the corresponding position near the unheated end of the beam.

The results of a typical experiment are given in Figure 1. An empty absorption tube was heated 9° above room temperature, 28° C., and temperature differentials between the end knives were read with a 40-gage copper-constantan thermocouple connected to a critically damped galvanometer showing a deflection of 1 mm. for 0.0004° C. In the first series of observations the pans were unloaded and zero point deflections and temperature differentials were recorded as nearly simultaneously as possible. These are plotted with white circles. In the second series of observations all conditions were the same except that the pans were loaded with 20 grams. The zero point deflections and temperature differentials are plotted with black circles. Both temperature differentials and rest point displacements are plotted as ordinates against time as the abscissa.

Examination of the curves in Figure 1 will show that an initial thermocouple deflection of 0.01° corresponds roughly to an error of 1 microgram but that the thermocouple equilibrates more rapidly than the beam. From this it may be concluded that temperature differentials as great as 0.01° between the ends of the beam are not to be tolerated. This is in general agreement with the calculations of Manley (*18*). The course of the thermocouple decrements in the two experiments serves as a control upon the accuracy of the reproduction of the conditions. In perfectly matched pairs of parallel experiments the two lines should be identical.

The curves show that after 200 seconds the air current produced by the slightly warmed absorption tube caused a shift of 63 micrograms in the rest point. Lengthening of the beam compensated this to the extent of about 10%, 7 micrograms, at zero load and more than a third, 23 micrograms, at full load. After 10 minutes the shift due to the air current had fallen to 21 micrograms, which was one-sixth compensated by the lengthening of the beam at zero load and 50% compensated at full load. Approximately 20 minutes were required for the heating error caused by the tube to disappear.

Obviously, the relative magnitudes of the air current effect and the expanding beam effect depend upon such factors as the size of the surface exposed to the rising air current, the presence of mechanisms which may act as baffles for the air stream, and the

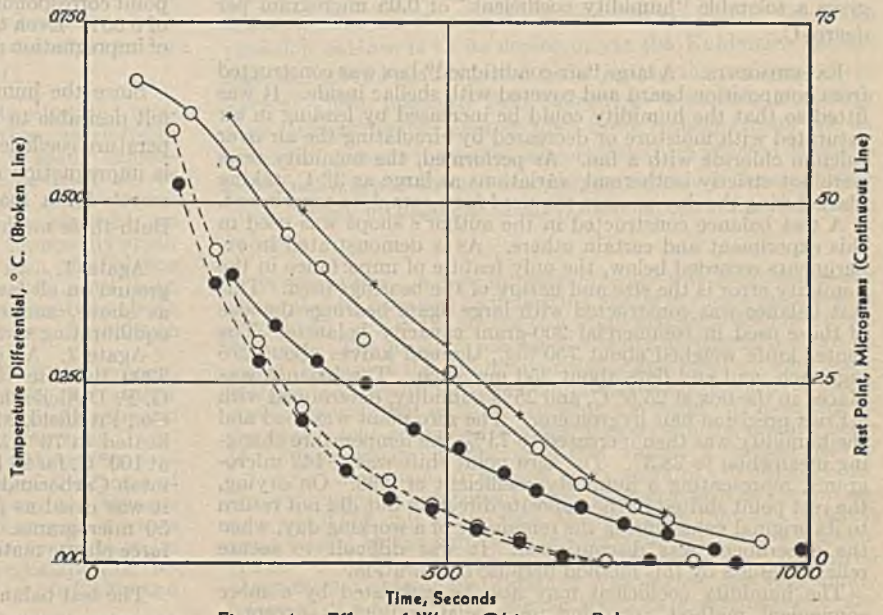

Figure 1. Effect of Warm Object on Balance

First series, unloaded pans: —○—○— rest point displacement; --○--○-- temperature differential.
Second series 20-gram load: —●—●— rest point displacement; --●--●-- temperature differential.
—x—x— rest point displacement extrapolated to zero load on knife.

thermal reflectivity of the beam. The author has been able to construct baffles so that the rising air current pushes the beam up from its tip but does not heat it appreciably, turns at the top, and gently descends to heat the arm on the opposite side. In this case the effects reinforce each other. Top and bottom compartments of the type recommended by Manley (*20*) are effective in preventing the heating of the beam but do not entirely remove the effects of temperature gradients on the zero point, since air currents in the lower compartment containing the pans can still affect the pans directly.

From the foregoing discussion, it can be seen that temperature gradients in the balance case can easily cause errors as large as 100 micrograms, thus necessitating the waiting period after loading which is recommended by Pregl. Further, even with a balance which does not permit a temperature gradient to arise from external heating in the laboratory atmosphere, the 5-minute period ordinarily recommended after a brief cooling might not be sufficient for complete temperature equilibration. With a poorly insulated balance, equilibration may never take place except momentarily by chance. Finally, the absolute magnitude of the effects due to gradients in temperature depends upon the details of construction of the balance but gradients as large as 0.01° are certainly to be avoided.

HUMIDITY COEFFICIENT

Changes in temperature ordinarily bring with them changes in relative humidity. Hence, if an instrument possessed a humidity coefficient, this would affect the results obtained upon exposing it to temperature changes. The importance of humidity control in weighing glass was recognized by Dumas and Regnault in early gas density determinations (*7*, *30*). The weight of skins of moisture on glass was determined by Manley (*21*) and on metallic surfaces by Strömberg (*36*). Since laterally unsymmetrical effects due to humidity changes are conceivable, it is necessary to evaluate the humidity coefficient of a balance before it is possible to evaluate its temperature coefficient accurately.

If we assume that changes in weight of absorbing materials are linear with relative humidity, we shall have a convenient basis for comparison of results and for the setting of tolerances. Since it has been observed that atmospheric humidity may change as much as 10% per hour and since we wish no error as large as 1 microgram, we may set as an acceptable tolerance that a balance may shift 0.5 microgram with 10% change in humidity. This gives a tolerable "humidity coefficient" of 0.05 microgram per degree C.

Experiments. A large "air-conditioned" box was constructed from composition board and covered with shellac inside. It was fitted so that the humidity could be increased by leading in air saturated with moisture or decreased by circulating the air over calcium chloride with a fan. As performed, the humidity tests were not strictly isothermal, variations as large as 3° C. taking place during the day or more required for a complete experiment.

A test balance constructed in the author's shops was used in this experiment and certain others. As is demonstrated in experiments recorded below, the only feature of importance in the humidity error is the size and nature of the bearings used. This test balance was constructed with large agate bearings the size of those used in commercial 200-gram capacity balances. The center knife weighed about 750 mg., the end knives about 275 mg. each, and end flats about 250 mg. each. The balance was placed in the box at 25.5° C. and 25% humidity, determined with a Friez precision hair hygrometer. The zero point was read and the humidity was then increased to 73%, the temperature changing meanwhile to 28.3°. The zero point shift was +142 micrograms, representing a humidity coefficient of 2.96. On drying, the rest point shifted in the opposite direction but did not return to its original value during the remainder of a working day, when the experiment was discontinued. It was difficult to secure reliable results by this method because of vibration.

The humidity coefficient may also be estimated by a more convenient method, requiring no special equipment except a hair hygrometer. The initial humidity and zero point are determined and then two sponges moistened with 5 to 10% sulfuric acid 2 to 3° above room temperature are placed in Petri dishes or watch glasses arranged symmetrically with respect to the pans inside the balance case. The case is closed and the balance is allowed to stand for at least 2 hours to equilibrate. Zero point readings are taken until no change is observed on 15 minutes' standing. The values of humidity and zero point are then recorded. Occasionally several hours are required for complete equilibration.

When the foregoing experiment was performed upon a Kuhlmann balance, the zero point shifted 15 micrograms on going from 20 to 90% relative humidity. This is a remarkably small change but not a negligible one if accuracy to 1 microgram is essential, since the coefficient is 0.214 or four times the tolerable coefficient chosen above. Drying the balance case caused the zero point to return slowly to its original value but 2 days were required before the process was complete.

It is possible to demonstrate that the humidity coefficient is due to the hygroscopic nature of the bearings, being almost entirely caused by the fact that water absorption by one end bearing is not exactly compensated by that of the other end bearing. This demonstration is accomplished by a series of experiments, described below.

An ordinary agate center knife was cleaned with acetone and placed in a drying chamber under oil pump vacuum for 4 hours at 100° C., then cooled to balance temperature under vacuum, and weighed as rapidly as possible. It was allowed to equilibrate with the atmosphere at 27% humidity and the gain in weight was found to be 603 micrograms. It is highly unlikely that two bearings made of this material would change by exactly equal amounts or at equal rates on humidification. Thus we have a possible explanation of the coefficient observed.

Two sets of end bearings, knives, and flats, selected at random from a large supply and identical in size with those used in the humidity test balance described above, were equilibrated against each other at 42% humidity and again at 83%. The excess change in weight over the change due to the balance itself was 152 micrograms. A balance with these knives would have had a coefficient of 3.71. This is comparable with that of 2.96 found in the test balance with similar bearings, showing that the observed humidity coefficient may be ascribed to unsymmetrical absorption of moisture by the end bearings.

It is not to be expected that any lack of symmetry in this respect in the center knife would seriously affect the result, since the average lever arm of the center knife is about $^1/_{60}$ of that of the end bearings and the moment resulting from an unsymmetrical change in weight of the center knife would be correspondingly small. That this is true can be demonstrated by removing the end knives and bearings from a balance and measuring its humidity coefficient when adjusted as a compound pendulum. A balance in this condition was adjusted back to its original sensitivity by lowering the center of gravity nut and its humidity coefficient determined. Between 41 and 80% the shift in zero point corresponded to a change of only 2 micrograms, a coefficient of 0.051. Even this small change may be removed by the process of impregnation described below.

Since the humidity error may be of such magnitude, it was felt desirable to reduce or eliminate it before studying the temperature coefficient. One possible method for reducing the error is impregnation of the agate with a wax or plastic, the other a search for a material of smaller intrinsic hygroscopic nature. Both these methods were tried successfully.

Agate 1. An ordinary center knife weighing 744 mg. was ground on all faces with 400-mesh Carborundum, cleaned, dried as above, and tested for hygroscopic gain as a control. On equilibrating at 30% humidity it gained 500 micrograms.

Agate 2. An ordinary center knife was refluxed in G. E. No. 3200 Bakelite "Monomer" (obtained through the courtesy of G. F. D'Alelio, head of the Plastics Laboratory, General Electric Co., Pittsfield, Mass.) for 24 hours, removed, and wiped. It was heated to 70° C. for 7 hours to remove alcohol and then cured at 100° C. for 24 hours. It was then ground on all faces with 400-mesh Carborundum to remove the resin on the surface. Finally it was dried as above and tested. On humidification it gained 50 micrograms. This experiment shows that it is feasible to force plastic materials into the pores of agate by this method.

The test balance used with plain agate in the earlier humidity experiment was fitted with knives and stirrup flat bearings impregnated as described for agate 2 and sponges were added to increase the humidity. Changing from 38 to 90% humidity

caused a shift of 72 micrograms. This is a coefficient of 1.38 as compared with 2.96 found with the same balance with untreated knives. This represents an improvement over the earlier performance of the balance but not a satisfactory result. After repeated reimpregnation of these bearings it was found possible to reduce the humidity change to 5 micrograms with 50% gain in humidity, a coefficient of 0.10 or twice the tolerance. The process of impregnation improved the performance of this balance with respect to humidity changes over that of the Kuhlmann, even though the Kuhlmann has the advantage of much smaller bearings.

Boron Carbide Flat. This was a trapezoidal bar 5–6 × 6 × 20 mm. and weighing 686 mg. It was cleaned with acetone, dried, and tested as above. No gain in weight with humidification could be detected. Unfortunately, the test balance could be fitted with a boron carbide bearing only in the center. Up to the present time the author has not been able to fit a balance with boron carbide bearings throughout.

It is thus seen that the low porosity of boron carbide makes it an ideal material for removing the humidity coefficient due to hygroscopic knives but that more than 95% of the difficulty can be removed by impregnation with Bakelite, thus making a carefully impregnated agate bearing system available for use in the determination of temperature coefficients. A detailed discussion of the preparation and performance of these and other bearing materials will be given in a subsequent communication.

Since the determination of the humidity coefficient of an operating balance is such an easy experiment, requiring only a good hair hygrometer and the inconvenience of withdrawing the balance from use for a day, it is earnestly recommended that as many users as possible perform this experiment to acquaint themselves with an important feature of the performance of their instruments.

SHIFTS CAUSED BY UNIFORM TEMPERATURE CHANGES

A balance containing repeatedly impregnated agate bearings and fitted with an all-aluminum case as a shield was placed in an air thermostat. The zero point was determined and the air bath was heated to 38–40° C. and allowed to equilibrate at this temperature. The zero point was then redetermined. Numerous experiments of this character were performed and many troublesome irreversible effects were discovered which will be treated in greater detail in a subsequent communication. On the other hand, reversible shifts in zero point in a beam free from irreversible shifts and from humidity errors were found to be very small, of the order of 1 to 2 micrograms per 10° C.

Manley (*24*) speculates as to the cause of the observed temperature coefficients of balances and ascribes them to shifts in the relative positions of adjusting screws. It is easily demonstrated, however, that balances containing force-fitted knives retain temperature coefficients. In 1926 Manley (*22*) reported observations upon the behavior of a balance made with an Invar beam and agate knives. In spite of the supposedly small coefficient of expansion of the material of the beam, the balance still had a relatively large "temperature coefficient". All these observations support the conclusion drawn experimentally above that the major portion of the temperature coefficient of a balance may be in reality its humidity coefficient.

In an exchange of correspondence with W. H. F. Kuhlmann, manufacturer of the Kuhlmann balance, in 1935, the author alluded to the small temperature coefficient of the Kuhlmann balance. Dr. Kuhlmann replied that several users had confirmed the small temperature coefficient of his balances as contrasted to other balances but that he had observed that some of his balances had greater sensitivity to temperature changes than others. He said that the source of this discrepancy was a mystery to him and that he had been unable to discover its cause. It should be noted that Schwarz-Bergkampf (*34*) reported a relatively large temperature coefficient for his Kuhlmann balances.

An examination of the Kuhlmann balance shows that it has a much smaller weight of agate in the end knives and stirrup flat bearings than other balances. The end knife is truncated to secure a lateral adjustment of parallelism with the center knife and the length and thickness of all end bearings are smaller than average. The flat bearings weigh less than 25 mg. and the knives weigh about 20 mg., making a total of about 45 mg. of agate in each end bearing as compared with 525 mg. in the test balance used above. Thus, if the humidity coefficients of both samples of agate were identical and the random match between the sets of end bearings equally good we should expect the Kuhlmann humidity coefficient to be 9% of 2.96 or 0.266 instead of 0.214 found. Better or poorer match between end bearings should give better or poorer coefficients, accounting for the observed variations.

These facts account for the remarkably small humidity coefficient actually observed on the Kuhlmann balance tested here and, in the opinion of the present author, they also account for the balance's small "temperature coefficient". The author's experiments with impregnation indicate that a single impregnation of the Kuhlmann agates should bring the humidity coefficient very close to the tolerance chosen. Thus three methods are open to the balance designer who wishes to produce an instrument with low humidity coefficient and low temperature coefficient: (1) use tiny agate bearings; (2) use more substantial agate bearings and impregnate them; (3) construct all bearings of a material like boron carbide which is insensitive to humidity changes.

Still another temperature effect should be pointed out in this section. The usual practice in balance construction is to make the beam from metal with a fairly high thermal coefficient of expansion and the knives from agate or other material of low coefficient. When a beam so constructed is subjected to extreme temperature changes, strains may be set up which will permanently affect the adjustment of the knives. Thus a Kuhlmann balance was exposed to an outside temperature of −21° C. overnight and when it was allowed to regain room temperature it was found that the sensitivity-with-load relationship was permanently changed, the sensitivity at full load being only 60 instead of 100 micrograms. This shows that it is not desirable to ship precision balances during extremely cold weather.

MAGNETIC INFLUENCES

The possibility that variations in the earth's magnetic field might influence the zero point of a balance was apparently first appreciated by Manley (*21*), whose Invar beam was ferromagnetic. An appreciable error due to the use of steel bearings was also found by McBain and Tanner (*15*) in a more sensitive balance. The use of magnetic material in the moving parts of a precision balance is to be deplored, yet the Kuhlmann balance has steel screws that are used for adjusting the positions of the knives. Since magnetic field changes in a modern laboratory may be considerably greater than those resulting from the diurnal variations in terrestrial magnetism which affected Manley's instrument, it was deemed necessary to determine the magnitude of the effect of magnetic field variations upon the Kuhlmann balance.

Experiments. A tangent galvanometer was modified by the removal of its base and its indicating needle in such a fashion that it could be used as the source of a small magnetic field of known intensity. The large coil was supported in a horizontal position on top of the case of the Kuhlmann balance and readings were taken without the current flowing and immediately afterwards with the current flowing but without arresting the beam. Duplication of the experiment gave results concordant within the reading error of the instrument. Imposing in this manner a vertical field of 1.7 c.g.s. units caused a zero point shift of 10 micrograms. Since the vertical component of the magnetic field at the laboratory was 0.552 unit at the time, the deviation from the true rest point caused by the vertical magnetic component was 3.3 micrograms. J. A. Fleming, director of the Department of Terrestrial Magnetism, Carnegie Institution of Washington, has very kindly informed the author that during times of great magnetic disturbances variations as large as 0.02 c.g.s. unit are found in Washington. Using this figure, we should calculate a maximum disturbance of 4% of the total force or 0.1 microgram, due to variations in the vertical component.

The experiment was repeated with the coil of the tangent galvanometer encircling the case of the Kuhlmann balance at the center and in a vertical position, thus creating a horizontal field parallel to the beam. Imposing a field of 2.28 units caused a change of 69 micrograms. Since the horizontal component of the field at the laboratory was 0.207 unit at the time, the permanent deviation from the true rest point caused by this field was 6.5 micrograms, corresponding to a maximum variation of 4% of this amount or 0.24 microgram.

It is thus apparent that the degree and distribution of residual magnetism in this particular beam are such that the errors caused by the earth's magnetic fluctuations are smaller than 1 microgram. On the other hand, magnetic fluctuations caused by electrical installations such as motors, generators, rheostats, or resistance furnaces may be many times those of the earth. An analyst using a Kuhlmann balance or any other with magnetic parts in the vicinity of electrical installations would have to take precautions to ensure protection against this effect. This could probably be most easily achieved by the use of a soft iron screen of high permeability and low retentivity.

The magnetic error of the Kuhlmann balance is small in a vertical field because the magnetic screws are symmetrically placed with respect to the knife in the horizontal direction. Thus vertical fields bring about only small torques due to differences between the screws with respect to residual magnetism. The relatively large sensitivity to horizontal fields is caused by the fact that in the vertical direction the screws are unsymmetrically placed, exerting a considerably greater torque above the knife than below it. Occasionally, analytical balances have been found with magnetic pointers. These would cause more serious errors due to the large moment which would be exerted by a force at such a distance from the knife edge.

OTHER ENVIRONMENTAL EFFECTS

Changes in barometric pressure can affect results only if the materials of the two sides of the balance are of different density. Such differences are seldom observed in balances themselves but are regularly found in microchemical weighings, due to faulty taring. Taring by the Pregl method can give rise to errors as large as 100 micrograms or more in a single absorption tube if the barometric pressure changes by 20 mm., a change which has been observed in this laboratory on more than one occasion during storms. The importance of proper taring has been fully understood by chemists for many years and satisfactory methods were developed by Regnault (*30*) in 1845 to permit the determination of gas densities. Discussions of the applications to microchemical weighings can be found in articles by Friedrich (*8*), Williams (*38*), and MacNevin and Varner (*16*).

The effect of tilting of the balance support was pointed out by Manley (*24*), while vibration has been discussed by Kirner (*13*) and Howard (*12*). Further comments on these subjects will be made in a later communication.

Errors Entirely Resident in the Instrument

The instrumental errors which are independent of environmental changes fall into two classes. Most of them are random errors which may be treated by statistical methods. These have been applied by Corner and Hunter (*6*) and the methods used in the author's laboratory do not differ essentially. Two do not fall into this category and will be discussed separately.

Data and Statistical Method Used. The primary objective of the statistical procedures followed in recording the observations below is not to evaluate errors accurately but to locate them and to make possible their reduction or elimination.

In the accompanying tables are recorded the number of observations, the standard deviation, σ, and another measure of reliability which seems appropriate for the purposes of the investigation, designated as E_{99}, defined as $E_{99} = 2.65\ \sigma$. If we assume a normal Gaussian distribution of errors, the probability is that 99% of the errors are less than E_{99} and only 1% is greater. Since many of the errors studied approach normal distribution fairly closely, a deviation of the magnitude of E_{99} will encompass practically all the valid observations. This measure is adopted because of the custom frequently followed by analysts and recommended in standard works on microchemical procedure of permitting the balance to stand for a predetermined time after closing the case, then releasing the mechanism and making a single observation of the deflection from three readings of the pointer. Assuming that there is no drift in the balance but that only random errors are at work, what is the maximum error to be expected from this procedure? The answer to this question is the real test of the validity of the procedure.

While the criterion, E_{99}, might appear to be unreasonably rigorous, it should be remembered that the determination of carbon and hydrogen requires six weighings and so, on an average, one out of seventeen analyses will be affected with an error of this magnitude or greater. On the other hand, the chances that errors of this magnitude will affect more than one weighing in an analysis are negligible.

Standard deviations have been calculated by the use of the formula

$$\sigma = \pm\sqrt{\Sigma(v^2)/(n-1)}$$

where v is the variation of each observation from the mean and n is the number of observations.

Many of the sets of observations recorded have been found to approximate roughly a Gaussian curve and others to represent a curve only slightly skewed. It follows immediately that the simplest method for increasing the accuracy of results in microanalysis is to adopt the time-honored device of making a larger number of observations than one and to use the arithmetical mean. The observations recorded in the following sections will give an idea of the efficacy of the statistical method in improving the precision of the weighings in various circumstances and of the limitations of the method as applied to balances commercially available.

Table I. Reading Error

No. of Observations	σ, γ	E_{99}, γ
14	0.8	2.1
10	1.3	3.4
10	0.8	2.1
10	0.9	2.3
10	0.8	2.1

READING ERROR

It is obvious that the process of interpolation commonly employed in estimating the pointer reading to 1 microgram on commercial balances will cause an error whose magnitude will vary with the operator and with the conditions of the observations. To dissociate this error from all others is very difficult, yet an estimation of its magnitude must be obtained in order to evaluate other errors.

The method adopted is to release the balance so that it has a moderate amplitude of oscillation and to record a series of ten or more successive deflection determinations, each calculated as usual from three reversal points. If the ten show a marked drift, the error can usually be laid to unequal heating, as has been developed above. In this case the set is discarded for the purpose of evaluation of the interpolation error. If a sharp break is recorded in the series of deflection determinations, so that the values fall into two distinct series, the members of which agree closely, the error at the break is probably due to mechanical damage at the knife, as is developed below. In this case also the set is discarded. If neither drift nor break intervenes, it may be assumed that the residual errors are due to interpolation. A series of ten is probably not sufficient to estimate the error accurately, yet a series very much longer is difficult to procure, owing to decrement. Table I gives the results of five series of many determined by different observers in this laboratory on a Kuhlmann balance equipped with a concave mirror. Each observation is calculated from three reversal points.

According to these results, the observer who made the second series would not be justified in relying on a single interpolation as being more accurate than 3 to 4 micrograms. For general purposes we may assume that the E_{99} due to reading error is of the order of 2 micrograms. It follows immediately that the operator who wishes to assure microgram accuracy must provide himself with a balance that reads directly to micrograms and automatically eliminates the interpolation error. If such an instrument is not available, he must have recourse to multiple observations. The accuracy of the observations on the Kuhlmann concave mirror balance may be increased by the use of a mounted magnifier. Table II gives the results of two representative series on the same balance with a 1.5-power magnifier.

While errors of this magnitude would prevent attaining microgram accuracy by a nonstatistical method if a balance were otherwise perfect, the larger errors which accompany it in the Kuhlmann balance minimize the effect due to interpolation.

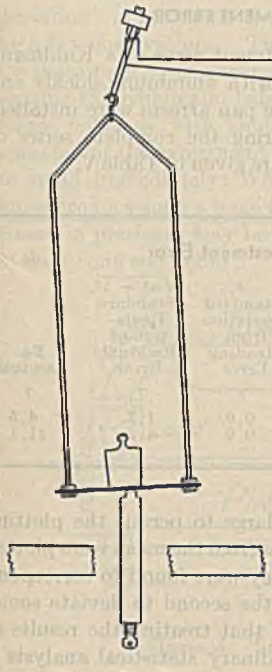

Figure 2. Stirrup

PAN ARRESTMENT ERROR

The pan arrestments upon the Kuhlmann balance are of fixed length, while the bows stretch when loaded. As a result, the distance from the stirrup arrestment to the bottom of the pan increases with increasing load. When the rigid pan arrestment touches the stretched, freely swinging pan, it tilts the pan and, consequently, the stirrup, as illustrated in Figure 2.

Table II. Accuracy of Observations

No. of Observations	σ, γ	E_{99}, γ
10	0.6	1.6
10	0.5	1.3

This effect may occasionally be avoided if the center of gravity of the pan and load system falls exactly above the pan arrestment. The farther the load is from the arrestment, the more difficult it will be to secure this adjustment. This leads to difficulties in weighing absorption tubes which are ordinarily placed some distance above the pan arrestment. Even if the center of the pan-load system is above the pan arrestment, the mechanical instability of this system with respect to its point of support makes it impossible to secure uniformly reliable vertical lifting. Any tilting causes an error upon the subsequent releasing of the beam, due to faulty replacement of the flat bearing on the end knife. The magnitude of the error is dependent not only upon the load but upon the method of loading. The error was examined by statistical procedures similar to those set forth in succeeding sections. In one series of observations the pans were arrested and in an otherwise identical series the pan arrestments were removed. This error does not follow a Gaussian probability curve at any load. With 9-gram absorption tubes it appears to have a "standard deviation" in the neighborhood of 1.5 micrograms, corresponding to E_{99} of 3.9 micrograms. Closer evaluation is of little interest because the error may be eliminated by substituting flexible arrests for the fixed arrests provided by the manufacturer. A simple design for such arrests is shown in Figure 3. For safety, the arrestment should be compressed by loads of less than 1 gram.

The author was not able to find spring wire sufficiently fine to give the delicate touch desired, but found that small lengths of sponge rubber are satisfactory for this application. These are cut so small in diameter that they slide in and out freely. They support a cylindrical pin which moves up and down in the hollow cylinder of the arrestment as impelled by the motions of the pan.

ERROR OF THE CENTER BEARING SYSTEM

Because temperature inequalities strongly affect the zero point of a balance, a Kuhlmann balance was equipped with aluminum shields to prevent body heat from causing temperature changes and with a 20-cm. (8-inch) extension handle for manipulating it from a distance. As changes in the rider could also cause shifts in zero point, the rider was not touched during a long series of observations. Elaborate systems of baffles were also installed in efforts to prevent fluctuations due to possible eddy currents set up by the motion of the beam. All these precautions were insufficient to prevent a considerable residual error on simply arresting and releasing the beam.

By means which are given in detail below, it was possible to establish the fact that this error was due mainly to the operation of the arresting mechanism. Accordingly, the pans and stirrups were removed and the balance was treated as a pendulum, with only its center bearing system in operation. Since the pans of the Kuhlmann balance were found to be unequal in weight, it was necessary to correct the equilibrium adjustment by about 200 mg. This cannot be accomplished with the equilibrium nut, even by moving it through the entire length of the threaded section of the bar which carries it. The support of the threaded bar itself can be rotated about its vertical axis, however, and by thus rotating the bar away from its normal position parallel to the beam, the beam could be balanced roughly with the adjusting nut and more accurately with the rider. A typical series of observations with the balance in this condition is given in Table III. All the precautions mentioned above were observed during this experiment.

Figure 3. Flexible Arrest

In this particular balance, then, the standard deviation of the residual error at the center bearing alone is of the magnitude of 1.2 micrograms, even when loaded with 15.8 grams less than the minimum load under service conditions.

The identification of the residual error of the Kuhlmann balance as an error of the center bearing system can also be achieved by a simpler manipulation of the balance. It is a fairly easy matter to lower the end arrestments so that they just miss the arrestment points on the stirrups. Under these conditions there can be no relocation of the positions of the flat end bearings with respect to the knives if the pans are not touched. To make sure of this point, it is necessary to lower the pan arrestments so that they do not touch the pans. The residual arrestment error found

Table III. Center Bearing Error

No. of Observations	a, Standard Deviation γ	E_{99} γ	b, Standard Deviation from Reading Error γ	$\sqrt{a^2 - b^2}$, Standard Deviation of Residual Error γ	E_{99}, Residual γ
10	1.5	3.9	0.9	1.2	3.2

Table IV. Center Bearing Error

No. of Observations	Load	a, Standard Deviation	E_{99}	b, Standard Deviation from Reading Error	$\sqrt{a^2 - b^2}$, Standard Deviation of Residual Error	E_{99} Residual
	Grams	γ	γ	γ	γ	γ
10	39.9	0.78	2.0	0.63	0.46	1.2
10	79.9	1.00	2.6	0.63	0.78	2.1

by this method, as described below, must be mainly due to operations at the center bearing (see, however, the last section of this paper).

If the error in the center bearing system were due to a shift in the relative positions of the center of gravity of the beam and the parts of the knife which support the beam, successive releases of the beam would cause errors which should increase in proportion to the increase in load on the center bearing. That this is approximately true is shown from the experiments recorded below.

Experiments. A factory-reconditioned Kuhlmann balance which had been used for student weighings was the subject of the following observations. The reading error had been reduced by the use of a magnifier in addition to the concave mirror supplied by the manufacturer. The stirrup arrestments were lowered, so that neither touched its corresponding arrestment points, and the pan arrestments were disconnected. It was found that the total load on the center knife when the pans were unloaded was 39.9 grams and when fully loaded, 79.9 grams. The balance was shielded with aluminum and was operated with a long handle. The rider was not moved during the observations. The results are recorded in Table IV.

$0.78\ \gamma \times 39.9/79.9\ \gamma = 0.39\ \gamma$ instead of $0.46\ \gamma$ found. These figures give a false sense of accuracy, since only the first digits after the decimal are significant. It can be concluded that the increase in the residual error is roughly in proportion to the increase in load. Since it is improbable that the error is due to any mechanical defect at the end knives under the conditions of the experiment, it is reasonable to conclude that it is due to a small shift in the point of suspension of the beam with respect to the center of gravity or, in other words, to an error in the center bearing system.

A third method for locating and roughly evaluating this error is given under Total Beam Arrestment Error.

We may thus conclude that in the Kuhlmann balance there is a residual error after correction for the error of interpolation, even when the center bearing is the only one in operation, as well as under conditions which make it improbable that there will be any end-bearing error.

A careful examination of the beam showed that no parts were loose and that the pointer always returned to the same point of the scale on arresting, thus showing that the error was not caused by a loose arrestment. This same error has been observed on numerous occasions with experimental balances having imperfectly ground center knives. It is probably due to progressive microscopic disintegration of the knife bearing, caused by faulty polishing or subsequent chipping. This error was noted by Thiesen in 1886 (*37*) and was subsequently commented on by Heyl and Cook (*11*). Schmerwitz (*33*) has shown that changes in form do take place in the knives and this is also made apparent by the measurements recorded in the last section of this paper. Such progressive disintegration would be capable of causing a load-dependent error of the type found above.

Manley (*17*) made graphs of the rest point plotted against the number of oscillations of a balance in a study similar to that described here (Reading Error). In these plots he observed both drifts and sinuosities and ascribed both to unequal heating effects. The author agrees, on the basis of experiments described under Error Due to Temperature Gradient, that the drifts were probably due to temperature gradients. He does not agree that sinuosities of the sort observed by Manley are to be attributed to temperature gradients, since experiments in this laboratory with much larger gradients failed to give sinuosities. He is more inclined to attribute them to imperfect bearings, a source of error which Manley overlooked. It will be noted in Manley's article on the subject that compartmentation stopped the appearance of the sinuosities, an effect ascribed by him to a marked reduction in temperature gradients in the vicinity of the beam. Actually, the sinuosities developed in a Bunge balance, and the beam was protected in a Gallenkamp balance, so that there is no basis for comparison of the effects with and without compartmentation.

Manley also attributed discontinuities of the sort observed by Thiesen and by Heyl and Cook, referred to above, to shifting of adjusting screws. The author has observed the same effects frequently in balances without any adjusting screws and thus feels that they are more properly ascribed to defective bearings.

TOTAL BEAM ARRESTMENT ERROR

To evaluate the total beam arrestment error of a Kuhlmann balance, the balance was shielded with aluminum shields and operated with a long handle, flexible pan arrests were installed, and the rider was not touched during the complete series of observations. The values obtained are given in Table V.

Table V. Beam Arrestment Error

No. of Observations	Load on Pan	a, Standard Deviation	E_{99}	b, Standard Deviation from Reading Error	$\sqrt{a^2 - b^2}$, Standard Deviation of Residual Error	E_{99} Residual
	Grams	γ	γ	γ	γ	γ
100	0	1.9	4.9	0.9	1.7	4.5
100	20	4.3	11.2	0.9	4.2	11.1

These two series are sufficiently large to permit the plotting of probability curves. The deviations from the mean were plotted in each instance. In the first set they were found to correspond well with a Gaussian curve and in the second to deviate somewhat. We may therefore conclude that treating the results of observations on this balance by ordinary statistical analysis is a reasonable procedure.

Careful examination of this balance shows that the manufacturer has supplied it in such adjustment that the left flat stirrup bearing is never separated from the corresponding knife bearing. Only the right stirrup bearing and the center knife are separated from their corresponding bearings when the arrestment mechanism is operated. An inquiry addressed to Dr. Kuhlmann elicited the information that all his microbalances were adjusted in this manner when they left the factory. Accordingly it is to be anticipated that any mechanical defects in the placement of the end bearings on release after arrestment would affect the right bearing only. On this assumption, the magnitude of the errors affecting the center and right bearings may be calculated.

If we represent the center bearing error by a and the right bearing error by b, both values taken at zero load on the pans, the increased error on the center bearing due to loading will be $(79.9/39.9)\ a$ and the increased error on the end bearing due to loading will be $(27.9/7.9)\ b$. (The weight of a pan and a stirrup is 7.9 grams.) We may then solve the following equations:

$$a^2 + b^2 = 2.80 \text{ (square of the residual error at zero load)}$$
$$(79.9/39.9)^2a^2 + (27.9/7.9)^2b^2 = 17.68 \text{ (square of residual error at full load)}$$

Solving, $a = 1.43$ (center bearing error at zero load on pan)
$b = 0.87$ (right bearing error at zero load on pan)

The value thus obtained for the center bearing error is of the order of magnitude found at a different time on the same balance by the method summarized in Table III.

It cannot be argued that the bearing errors found on arrestment and recorded here are peculiar to the particular balance investigated in this laboratory, since the author has had an opportunity to investigate sixteen Kuhlmann balances in various laboratories and has found all to have errors of the same order of magnitude.

The conclusion that the end bearing which is arrested is affected by an error due to the operation of arresting may be vividly demonstrated by raising the arrestments under the left stirrup points until both stirrup bearings arrest when the mechanism is operated. Observations with this adjustment are:

No. of Observations	Load on Pan	Standard Deviation γ	E_{99} γ
10	0	11.3	29.5

When the pans are loaded, the magnitude of the error increases still further. With such a large error, the "standard deviation" is not to be regarded as being closely approximated by a few observations. The highly erratic behavior summarized by these figures, however, shows that one of the major factors causing the Kuhlmann balance to perform more accurately than many balances with similar rudimentary arrestments is the omission of the arrestment of one bearing. Two questions come to mind immediately: Why does the arrestment of the third knife produce such a huge increase in error and what, if any, increase in precision may be obtained by omitting the arrestment of the second end knife?

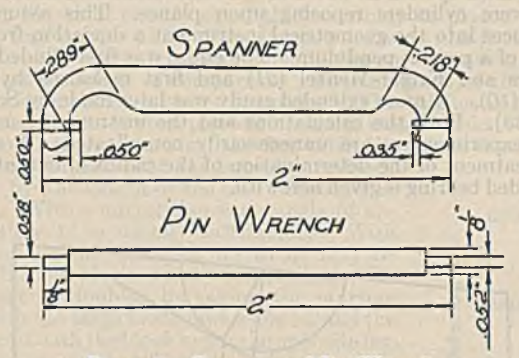

Figure 4. Spanner and Pin Wrench

The motion of the beam may be examined under a microscope at any point desired by mounting a horizontal microscope near the point of interest and a sheet of paper back of that point with sufficient illumination to make the silhouette visible. Such an examination at the moment of arrestment shows the reason for the huge error when both end knives are arrested. With the straight fall-away type of arrestment characteristic of the Kuhlmann balance, it is impossible for the mechanism to arrest all three knives without lifting the end bearings first. If the center bearing were arrested first, the beam would be lifted at the same rate as the arrestment arm and at least one of the stirrups would never be overtaken. Arresting the end bearings first necessarily results in lifting the bearings while the beam is oscillating. This causes violent chattering motion which is plainly visible under the microscope. Hence this elementary type of arrestment is not satisfactory when the manufacturer desires to extend the protection of arrestment to all three bearings.

Curiously enough, the same argument does not apply when only two bearings are arrested. By making the left pan and stirrup combination heavier than the right, the oscillation of the beam may be terminated by catching the beam with the two end arrestments before any knife is lifted. The right knife is then lifted immediately. The weight of the left stirrup in contact with its knife prevents the beam from oscillating further and the whole beam is finally lifted from the stationary center bearing. This gives a tremendous improvement in the arrestment action, but observation with the microscope shows that chatter is not entirely eliminated. As a result, the knife which is arrested, supposedly as a precautionary measure to protect it, suffers incessant pounding during the process. As is demonstrated below, this actually causes it to deteriorate more rapidly than the knife which is not "protected" by an arrestment. Thus, in this instance, a faultily designed arrestment was worse than no arrestment at all.

An increase in both accuracy and lifetime of the Kuhlmann balance may be secured by readjusting it so that neither end arrestment works and both knives remain permanently in contact with their flat bearings. To accomplish this, two special tools, a spanner and a pin wrench, shown in Figure 4, are required. The other end of each wrench is made to fit similar parts of the pan arrestment. These are located within the glass base.

The readjustment should be carefully performed, so that both arrestments come as close as possible to arresting without actually succeeding. The course of the readjustment may be observed by using a brightly illuminated sheet of white paper as a background for the observation of the contact or separation of each end flat bearing from its knife. The author's experience over a considerable period of years is that this single readjustment of the Kuhlmann balance is the most effective that can be made easily to improve its performance and that it eliminates essentially all of the end-knife arrestment error. This procedure is certainly to be regarded as a compromise due to faulty arrestment design. While it is highly desirable that all three knives of a balance should be arrested, careful experimentation has revealed no method for accomplishing this without sacrifice of accuracy on the Kuhlmann balance short of building in a complete new arresting system.

Another change which will improve the action of the arresting mechanism is the installation of a Conrady pointer brake (*5*). This is a light wire mounted on knives near the pointer with a small arm to make contact with a moving part of the arrestment. It is adjusted to rub lightly against the pointer until after the knives are released and then to be swung free by the contact of the arrestment part on its arm. While this does not increase the accuracy greatly, it does assist in the protection of the arrested end knife, since its action is to stop the oscillation of the beam before the knife is lifted. The author recommends the use of a Conrady pointer brake with all precision balances to guard against accidental violent fluctuations of the beam.

To aid in comprehending the problem of mechanical design posed by microchemical balances, we may calculate the magnitude of the changes in arm length which are responsible for the observed end knife error on arrestment. Since the length of a single arm of the balance is 35 mm., the deviation in arm length which would be responsible for an error of 0.9 microgram at 7.9-gram load is $\frac{35 \times 0.9}{7.9 \times 10^6}$ mm. or 4 mμ. It is not surprising to find a balance with a random deviation in arm length upon arrestment of the order of 0.00000025 cm. (0.0000001 inch), yet it is obvious that this error must be traced and eliminated if the desired accuracy is to be attained.

Table VI. Rider Error

Experiment	No. of Observations	Standard Deviation γ	E_{99} γ	Standard Deviation of Residual Error γ	E_{99} Residual γ
(1) Reading only	10	(*a*) 0.5	1.3		
(2) (1) + arrest	10	(*b*) 0.78	2.0	$\sqrt{b^2 - a^2} = 0.6$ (center bearing error)	1.6
(3) (2) + rider adjustment	10	(*c*) 1.6	4.2	$\sqrt{c^2 - b^2} = 1.4$ (rider error)	3.7

RIDER ERROR

The presence in the Kuhlmann balance of an error due to inaccurate placement of the rider in the notches of the beam has been commented on by Ramberg (*29*) and Schwarz-Bergkampf (*34*). To eliminate this error a bar rider with channel beam has been introduced by Seederer (*35*) and Gattoni (*9*) of the Seederer-Kohlbusch Co. A similar device has also been proposed by Ramberg and introduced abroad by the Sartorius Werke (*14*). Since most commercial balances are not designed to eliminate the rider error, its magnitude must be evaluated in order that the performance of the balance at all loads may be understood. This may be accomplished by making two series of observations.

the first in which the rider is never moved, the second in which it is reset as accurately as possible after each reading. The usual statistical treatment then permits calculation of the error. A typical experiment of this sort is recorded in Table VI. The experiments were performed on a Kuhlmann balance shielded against body heat and with neither end bearing arresting.

The observations recorded above represent the errors to be expected in weighing a sample on a greatly modified Kuhlmann balance under ideal conditions. Heat errors were eliminated, pan arrestment and end bearing arrestment errors were not present, and great care was taken with each setting of the rider to secure the best adjustment which could be made by eye. This experiment has been repeated on numerous occasions with closely concordant results.

Figure 5. Contact of Knives with Flat Bearings

By a further modification of the balance, even the rider error may be eliminated. The substitution of a 0.5-mg. or 1.0-mg. rider for the 5.0-mg. rider ordinarily supplied with the Kuhlmann balance eliminates the rider error but makes it necessary for the analyst to use milligram weights. If real accuracy is desired, this procedure is recommended. Under these conditions, accuracy of the order of magnitude of that given in the second experiment may be achieved.

Schwarz-Bergkampf (*34*) examined a Kuhlmann rider bar for differences in the machining of the notches and found none great enough to affect weighings. Manley (*23*) notes that errors in machining rider bars do occur, however, and recommends that the user provide apparatus to protect himself against such errors. The process of checking the accuracy of machining of a rider bar may be accomplished in at least two different ways. Use of a microscope with an ocular micrometer, as described by Schwarz-Bergkampf, is not thoroughly reliable, since progressive errors might be missed. A better method is to use a microscope mounted on a micrometer screw of sufficient length to cover the entire beam without resetting. A simpler method which is open to the analyst is to construct a 50-mg. rider of platinum with as nearly as possible the dimensions of the Kuhlmann rider. The rider bar may then be calibrated by balancing each new setting of the rider with milligram weights. Only the former method has been used in this laboratory. The Kuhlmann beam was measured with a 100-mm. Gaertner micrometer microscope and 39 notches were found to deviate 1 microgram or more from the average while 8 deviated 2 micrograms or more. None was off by 3 micrograms. The cumulative error was 2 micrograms at the fiftieth notch.

These measurements indicate that even better machining is necessary to secure true microgram accuracy. They are not thoroughly reliable, however, because of the impossibility of deciding by a microscopic examination the exact point at which the rider will seat. Some of the notches had appreciable burr which would have thrown the rider off by more than the amount indicated by the microscope. This leads to the conclusion that rider notches should probably be ground and not milled, although a small burr from milling might be removed by subsequent grinding. The user who wishes to secure the greatest possible accuracy from his instrument should first examine all notches with a hand magnifier and remove any burr with a sharpened match stick, since this is too soft to affect the machining of the notch. He should then calibrate the notches with a platinum rider. Alternatively, the use of a lighter rider, as recommended above, eliminates the error on this particular type of balance.

Curvature of the Knives

The replacement of a flat bearing on a perfect knife should always yield the same arm length, even when the replacement is not performed with precision. One might inquire, then, why arrestment errors are possible. They would not be if actual balances were the same as the "geometrical balances" with which balance theory usually deals. For the purposes of the present argument, however, it is necessary to set aside the usual assumption that the knife bearings form perfect geometrical straight lines.

Figure 5 shows several possibilities of the contact of knives with flat bearings. In *a* we have the picture as it is usually represented, a perfect straight line in contact with a perfect plane. In practice this is impossible of attainment because of mechanical deformation. If we imagine a soft knife in contact with a hard flat, we shall have the type of contact shown in *b*. This case is frequently observed and gives rise to rapid dulling of the knife edge. A hard knife in contact with a soft flat gives the figure shown in *c*. This case is also easily demonstrated in practice and results in permanent injury to the flat bearing. Balances equipped with bearings of types *b* or *c* quickly show erratic behavior. An ideal combination is one in which both knife and flat bearing are constructed of the same material or materials of equal hardness and in which neither is loaded beyond its elastic limit. The picture of the deformation to be expected in such a case is shown roughly in *d* and is the case normally to be expected. If we permit the bearing shown in *d* to roll slightly, the depth of penetration will remain constant and the net effect will be that the circumference of the convex cylinder will move along a plane parallel to the original plane of the bearing but displaced from it by the distance of the depth of penetration. For this reason the figure may be simplified for the purpose of the analysis of the statics (but not necessarily the dynamics) of the balance system as in *e* and we shall treat the knives as if they were cylinders reposing upon planes. This assumption introduces into the geometrical instrument a deviation from the action of a perfect pendulum. The effect was first alluded to by Richarz and Krigar-Menzel (*31*) and first measured by Guglielmo (*10*). A more extended study was later made by Schmerwitz (*33*). Both the calculations and the instruments used by these experimenters are unnecessarily complicated. A simplified treatment of the determination of the radius of curvature of the loaded bearing is given herewith.

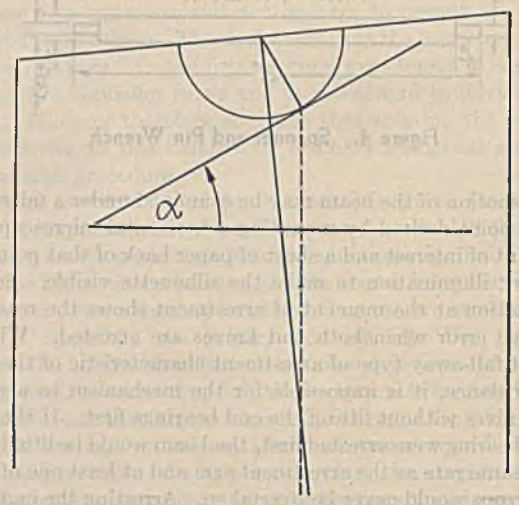

Figure 6

Tilting the case of a sensitive balance will cause the beam to incline from the horizontal until the center of gravity assumes a position below the point of contact of the bearing with the plane. This position is represented in Figure 6. Adding a restoring weight, w_r, will bring the beam back to the horizontal position as in Figure 7. Moments about the point of contact may now be equated. The mass of the beam is acting through the lever arm ($r \sin \alpha$). The restoring weight is acting through the lever arm ($L - r \sin \alpha$). Because ($r \sin \alpha$) is so small with respect to L, it may be neglected in the second expression. We thus have:

$$Mr \sin \alpha = w_r L$$

or

$$r = w_r L / M \sin \alpha$$

Procedure. In the laboratory, this method of tilting the balance case to determine the radius of curvature of the center knife is much simpler than the procedures described by Guglielmo and Schmerwitz. The tilting is accomplished by the use of gage blocks. If the balance is supported by three legs, two in front and one in back, it may be tilted sideways by the use of two gage blocks, one exactly twice as thick as the other. The thicker block is placed under one front leg, the thinner under the central stud in the rear of the case. If the balance is supported by four

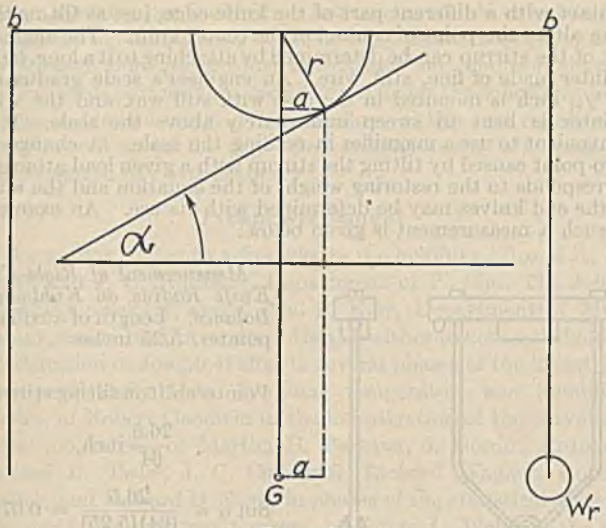

Figure 7

legs, two blocks of exactly equal thickness may be placed under the two legs on one side. The distance between the front legs is measured as accurately as possible, using corresponding parts of the legs as points of comparison. The thickness of the gage blocks is determined with a micrometer. The balance is set for the test on a glass or steel plate or upon flat metal blocks, so that the legs will not sink in when the case is tilted. Under these conditions the thickness of the largest gage block divided by the length of the case between legs is sin α. With a microbalance an angle of approximately 1° is usually satisfactory. With analytical balances, angles up to 3° may be used. If gage blocks for 1° are available, the angle may be doubled by taking the starting point with the large block under one leg and the tilted point with the block under the opposite leg.

When the case is tilted, the pointer scale is moved with respect to the gravity line. The pointer should, therefore, move through angle α on the pointer scale if the bearing were perfect. The difference between the angle through which the pointer should move and that through which it actually does move, translated into terms of weight, represents the restoring weight. Since the critical quantity desired is usually a small difference between two larger quantities, each reading must be made with the greatest precision of which the balance is capable.

To calculate the restoring weight, it is necessary to evaluate α in terms of pointer scale divisions. There are two methods for doing this. One is to measure the pointer scale and the distance to it from the knife edge and set their quotient equal to the sine of the total angle subtended by the scale. From this the fraction represented by angle α can be calculated. The other method is to lower the center of gravity of the beam a great deal, perhaps by attaching a light clamp to the pointer part of the way down, and then to tilt the case through angle α and see experimentally how far the pointer moves. With the center of gravity very low, the balance performs as a perfect pendulum with respect to the angle of tilt and the theoretical value can be read off directly from the scale.

The length of the beam can be measured conveniently and by dividing by 2 the arm length, L, is obtained. The mass of the beam is obtained by weighing it on a rough balance. If the balance has been prepared for the experiment by the removal of the pans and stirrups, only the mass of the beam is involved in the expression. When performing the determination in this manner, it is sometimes necessary to make a considerable readjustment of the zero point with the balancing nuts to bring the pointer to the scale. The determination may also be performed with pans and stirrups in place, but even in this case M is the mass of the beam only, provided that the sensitivity remains constant with load. That the radii of the end knives will not affect the result can be seen from Figure 7 if we imagine the point "end bearings" shown ($b - b$) to be replaced by cylinders with planes tangent at the same points as those in the illustration. This change will not affect the arm length. With the quantities found thus the radius of curvature can be calculated. An example of an actual determination is given herewith.

Measurement of Center Knife Radius of Kuhlmann Balance. Calculation of α in Pointer Scale Units.

Thickness of gage block, 6.35 mm.

Length of case, 339 mm.

$$\text{Sin}\ \alpha = \frac{6.35}{339} = 0.01873$$

Length of Kuhlmann pointer, 139 mm.

If the bearing were perfect, tilting the case through α should displace the pointer scale from the perpendicular position of the pointer by 139 sin α mm. or 2.604 mm. But 100 Kuhlmann scale units = 1.938 mm.

$$\text{Hence} \qquad \alpha = \frac{(2.604)(100)}{1.938} = 134.35 \text{ scale units}$$

Thus tilting the case through α should shift the scale by 134.4 units of rest point if the bearing were perfect. If we use deflection instead of rest point, tilting the case through α should cause a displacement in the deflection of the pointer of 269 scale units.

Calculation of the Radius of Curvature. The displacement observed on tilting through α was 205 scale units. This means that tilting the case caused a shift of the pointer from the perpendicular position of (269 − 205) or 64 scale units. The sensitivity of the balance was, 1 unit of deflection $= \frac{0.1}{108}$ mg. per scale unit $= \frac{1}{1080}$ mg. per scale unit. Hence 64 units $= \frac{64}{1080}$ mg. = 0.059 mg.

Weight of beam, 24,029 mg.

Length of arm, L, 35 mm.

Hence,

$$r = \frac{(0.059)(35)}{(24{,}029)(0.01873)} = 0.00456 \text{ mm. or } 4.6\ \mu$$

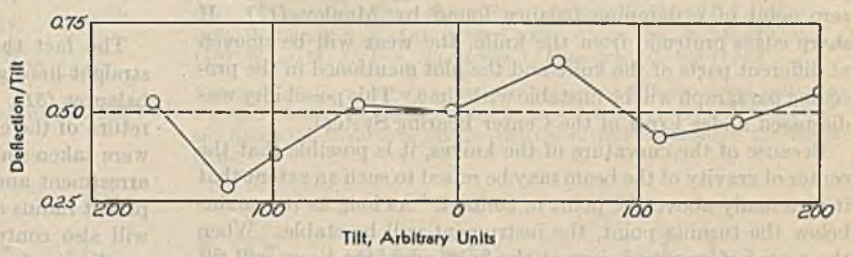

Figure 8. Curvature of Knife Edge
---- r = 11.2 μ

The equation for the calculation of the radius of curvature is the most important of all the expressions at present applicable to a precision balance because it enables the user to evaluate the constant which is most directly responsible for reproducibility in the instrument as contrasted to sensitivity. It is conceivable that a method may be found for preparing knives which are tiny perfect cylinders. However, at the present time, such a technique has not been described. Any larger radius of curvature than the minimum obtainable with the material used is to be regarded as a flaw and is always accompanied in practice by more or less erratic behavior on the part of the instrument. A subsequent communication will contain details upon the application of this test method to the preparation of precision knife-edges. As a result of these experiments, we regard 0.25 μ as being the maximum radius permissible in a precision instrument. It is to be emphasized, however, that this figure represents the maximum permissible when the objective of the manufacturer has been to produce a mathematical line for the bearing. If he were to find a process for preparing a perfect cylinder of slightly larger radius, this might actually be preferable.

If we consider that the center flat bearing of the balance is perfectly plane and the knife is ground to a mathematical straight line, the contact will be cylindrical, as shown in Figure 5, *d*, because of the mechanical deformation of the bearings under the load impressed upon them. In practice, this is the nearest approach to the ideal case. Actually, it is frequently found that the flat bearing deviates considerably from perfect flatness and the knives are not perfectly ground. Even in this case the equa-

tion given above provides a means for learning what the condition of the bearing is. An examination of Figure 6 will show that the angle of tilt of the beam produced by tilting the case through a given angle will be increased by raising the center of gravity. By raising it sufficiently, it is possible to make the balance so sensitive to tilt that the excursion of the pointer may be subdivided into a considerable number of angular increments. If the case be tilted through successive angular increments by means of a micrometer screw under one end, a curve may be constructed by plotting the deflection per unit tilt of the case against the number of micrometer units that the case is tilted. The value of the plot at zero is indeterminate. With a perfect cylinder this plot should be a horizontal straight line. If there are irregularities in the edge, the apparent radius of curvature will differ with different angular increments and the plot will not be a horizontal straight line. From the shape of the curve it is possible to reconstruct roughly the shape of the knife-edge. An example of the appearance of such a curve is given in Figure 8. The "radius of curvature" at any angle may be obtained by multiplying the ordinate at that angle by 22.4.

This procedure is suggested by the work of Guglielmo (*10*) and is much simpler than that of Schmerwitz (*33*). With either this procedure or that of Schmerwitz, the author has found it possible to locate deviations from the form of a perfect cylinder only with relatively poor knives.

It will be obvious immediately that an imperfectly ground knife-edge in the center bearing will cause the instrument to behave erratically. If the distance from the center of gravity to the point of suspension varies irregularly with the angle, the zero point of an oscillating balance will be irregularly dependent upon the amplitude of the oscillations. This is a possible explanation of the "sinuosities" of the curve of the zero point of a damping balance found by Manley (*17*). If sharp edges protrude from the knife, the wear will be uneven at different parts of the knife and the plot mentioned in the preceding paragraph will be unstable with time. This possibility was discussed under Error of the Center Bearing System.

Because of the curvature of the knives, it is possible that the center of gravity of the beam may be raised to such an extent that it is actually above the point of contact. As long as it remains below the turning point, the instrument will be stable. When the center of gravity is just at the knife-edge, the beam will tilt through the same angle as the case and the pointer will appear to remain fixed with tilt. These cases were pointed out by Conrady (*5*). While Conrady appeared to look with some favor upon the possibility of the preparation of precision balances with such adjustments, the author's experience has been that such an adjustment cannot be obtained in practice except with a very poorly ground knife and that a knife which is so poor as to permit adjustment to Conrady's "autostatic" state is so poor that it will not give reproducible weighings.

Radii of the End Knives

If the center knife were a perfect cylinder, its radius could be quite large without affecting the reproducibility of weighings. With the end knives the situation is different. Here each increase in radius of curvature carries with it the necessity for a corresponding increase in the precision of replacement of the flat bearings by the arresting mechanism, if precise weighings are to be obtained. Hence the problem of the tolerances to be set upon arrestment design is inextricably bound up with the radii of the end knives.

A manufacturer may determine the radii of the end knives by inserting them in a special balance as center knives before mounting them. This procedure is hardly available to the user of an instrument, who will be forced to resort to such a method as that outlined below.

Procedure. The compensating link of the stirrup is temporarily replaced by a special link which immobilizes the wrist action in the direction of the beam but permits the pan to swing freely in the direction perpendicular to the beam. This is illustrated in Figure 9. Hanging a weight on one side or the other of this special link will tilt the stirrup and cause it to come into contact with a different part of the knife-edge, just as tilting the case alters the point of contact of the center knife. The angle of tilt of the stirrup can be determined by attaching to it a long, light pointer made of fine, stiff wire. An engineer's scale graduated in $^1/_{64}$ inch is mounted in the case with stiff wax and the wire pointer is bent to sweep immediately above the scale. It is convenient to use a magnifier in reading the scale. A change in zero point caused by tilting the stirrup with a given load attached corresponds to the restoring weight of the equation and the radii of the end knives may be determined with its use. An example of such a measurement is given below:

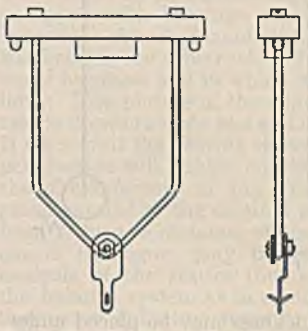

Figure 9. Radii of End Knives

Left, front view. Right, bent brass pin soldered in to hold pan and weights

Measurement of Right-End Knife Radius on Kuhlmann Balance. Length of auxiliary pointer, 5.25 inches

Pointer shift on tilting stirrup,

$$\frac{26.5}{64} \text{ inch,}$$

$$\text{Sin } \alpha = \frac{26.5}{(64)(5.25)} = 0.0789$$

The special stirrup with its load was adjusted to 10 grams. Shifting this weight through angle α caused a displacement of 0.288 mg. Hence $w_r = 0.288$ mg.

$$r = \frac{(0.288)(35)}{(10{,}000)(0.0789)} = 0.01278 \text{ mm.} = 12.8\ \mu$$

The fact that the end bearings are also not mathematically straight lines gives rise to the stirrup arrestment error noted in balances (*31*). Unless the mechanism is designed to secure the return of the end bearings to exactly the point from which they were taken on arrestment, the arm length will vary with each arrestment and weighings will not be reproducible. If the apparent radius of curvature varies with the angle, the end knives will also contribute to an irregular error dependent upon the amplitude of oscillation of the balance. This effect would be even more pronounced if the center of curvature varied with the angle. It is true that an imperfect bearing might give rise to a very small error, provided that the imperfection were exactly proportional to the angular displacement from the perpendicular. If, however, any point on the bearing surface had its center of curvature displaced horizontally from the average center of curvature by so much as 13 Å. it would cause an error of 1 microgram at full load on the Kuhlmann. This follows from the fact that at full load the end knife of the Kuhlmann has a load of 27,000,000 micrograms. To cause an error of 1 microgram would require a change in arm length of $\frac{35 \text{ mm.}}{27{,}000{,}000}$ or 13 Å.

When the Kuhlmann balance was first purchased, the author's examination showed that all three knives had radii between 3.0 and 3.5 μ. Six years later, the center knife had a radius of 4.5 μ and the left knife 5.2 μ, while the right knife showed a radius of 12.8 μ. From these results it will be observed that the left knife, which was not arrested, maintained its radius of curvature better than the right knife which was arrested. This emphasizes again the faulty nature of the Kuhlmann arresting mechanism.

In the examination of balances other than the Kuhlmann, certain of the errors enumerated above and still other errors not present in the Kuhlmann will be found. In view of the number of factors which can cause microgram errors, it is impossible to predict the probable accuracy of any balance without a thorough trial under the intended conditions of use. Since different instruments vary in their susceptibility to environmental influences and different laboratories vary widely in the suitability of their balance rooms for susceptible balances, various instruments will show wide divergences of performance in different laboratories.

The prospective purchaser of an instrument should calculate for himself the maximum error which he can tolerate in weighing and should then purchase an instrument only on condition that it can meet this performance specification under the conditions prevailing in his laboratory. Specifications of this sort rigidly adhered to will speed the day when manufacturers will cease to confuse sensitivity with accuracy.

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Colorimetric Determination of Tin with Silicomolybdate

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A rapid and accurate colorimetric determination of tin for concentrations ranging from 0.0005 to 0.5% is described. The method is an excellent routine procedure requiring no special technique or apparatus other than a comparator or filter photometer. Tin is separated by distillation and determined colorimetrically in the distillate. Five determinations can be run in 2 hours. Effects of variables such as time, acidity, and concentrations of reactants and of interfering ions have been investigated.

THE determination of tin, particularly in small concentrations, is of vital importance in analyses of steels and nonferrous alloys. Since much of our present steel is being prepared from scrap which may contain tin, and since the presence of tin even in small concentrations is likely to be injurious, added stress is placed on the determination of tin in steel and scrap. Generally, small amounts of tin, ranging from 0.001 to 0.05%, will be found in most steels with the exception of tinplate or special melts. The determination of small quantities of tin in food, biologicals, fumes, and organic matter is also important.

Since small quantities of tin are present in the material to be analyzed, gravimetric or volumetric procedures (*10, 14*) are unsatisfactory.

Spectrographic analysis (*9, 11*) offers an excellent solution to the problem. However, because of the skill and expense required, spectrographic methods are beyond the reach of the average laboratory.

An examination of colorimetric procedures suitable for the determination of tin in the concentration range of 0.0005 to 0.5% was undertaken. The use of organic reagents (*16*) for the colorimetric determination of metallic ions has increased considerably. Newell, Ficklen, and Maxfield (*8*) made a critical study of the use of cacotheline test and found that it cannot be regarded as specific. Where interfering substances are absent, the test may be used for detection or confirmation of the presence of small amounts of tin. Experiments with cacotheline in the authors' laboratory failed to give satisfactory quantitative results. Tartakovskiĭ (*12*) used hematoxylin for the colorimetric determination of tin. The concentration of tin required ranges from 0.3 to 2 mg. per liter of solution. The sensitivity is, therefore, too great to obtain accuracy in the ranges of tin concentration in which the authors are interested.

Hanssen (*2*) recommended comparison of colloidal tin sulfides. The method is unsatisfactory, since traces of elements and the presence of sulfur caused by the bromine used in the oxidation of stannous ion result in large deviations.

A number of other procedures have been suggested. Clark (*1*) used 4-methyl-1,2-dimercaptobenzene to determine 2.5 to 30 parts of tin per million parts of solution. Diazin Green S (K) (*16*) has been used to detect as little as 0.02 mg. of tin per drop of solution. Lowenthal (*6*) used a mixture of ferric chloride and potassium ferricyanide for the estimation of stannous ions.

Longstaff (*5*) used the reaction based on the reduction of ammonium molybdate by chlorostannous acid to detect tin to the extent of 1 part in 1,500,000. Hüttig (*3*) developed conditions under which he claimed quantitative results: separation of the sulfides of arsenic, antimony, and tin, dissolving in 1 to 1 hydrochloric acid, boiling to remove hydrogen sulfide, and reduction with zinc. The reduced tin solution is filtered into 100 ml. of an ammonium molybdate solution and after 0.5 hour is compared with a similar solution prepared from a standard tin solution. Attempts to duplicate these results in this laboratory failed.

EXPERIMENTAL WORK

In order to determine the cause of the erroneous results obtained using the method of Hüttig (*3*), an investigation similar to that of Truog and Meyer (*13*) and Woods and Mellon (*15*) on the molybdenum blue reaction was conducted. This included the effect of acidity, reagents, method of reduction, and time of reaction upon the color developed. The experiments were performed by adding a standard chlorostannous acid solution to an ammonium molybdate reagent solution.

Variations in the acidity of the solution under test caused divergent results at high acidities; the blue color of the reduced molybdate complex did not form. At lower acidities inconsistent results were obtained in the intensity and fading rates of the blue color. No conformity to Beer's law was found.

Table I. Colorimetric Determination of Tin

Tin Taken	Tin Found: Photometer[a]	Tin Found: Comparator[b]	Tin Taken	Tin Found: Photometer[a]	Tin Found: Comparator[b]
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
0.02	0.0196	0.022	0.50	0.500[c]	0.500[c]
0.04	0.0392	0.0415	0.60	0.573	0.562
0.08	0.088	0.085	0.70	0.670	0.685
0.10	0.096	0.090	0.80	0.787	0.766
0.12	0.140	0.131	0.90	0.851	0.862
0.16	0.171	0.176	1.0	0.952	0.948
0.18	0.184	0.187	1.1	0.965	0.960
0.20	0.241	0.231	1.2	1.06	1.07
0.30	0.284	0.290	1.5	1.14	1.11
0.40	0.364	0.378			

(Values through 0.18 mg. of Sn determined by micromethod)

[a] 0.5 mg. of Sn on A Scale Fisher AC electrophotometer using 650A filter = 22.5 mg.
[b] 0.5 mg. of Sn at 20 mm. on Duboscq comparator.
[c] Standards.

The ammonium molybdate reagent used by Hüttig (*3*) is prepared by dissolving 0.3 gram of C.P. ammonium molybdate in 4 ml. of water, adding 2.4 ml. of a 14 *N* sulfuric acid solution, stirring, and adding 3 ml. of a 2 *N* sodium hydroxide solution and 1 liter of water.

Preparation of this solution resulted in formation of a yellow color. An examination of the reagents and their impurities led to the conclusion that the yellow color was due to the formation of a heteropoly compound from the acid ammonium molybdate and the silica impurity in the sodium hydroxide. This was further verified by substituting an equivalent amount of silica-free potassium hydroxide for sodium hydroxide in the molybdate reagent in one experiment and in a second experiment omitting sodium hydroxide and adjusting the acidity by reducing the sulfuric acid content of the reagent. In every case where the silica was removed the yellow coloration did not appear and a very weak, unstable blue color was formed upon reduction of the molybdate reagent with the standard chlorostannous acid solution. Addition of a solution of sodium silicate to the silica-free reagents formed the yellow color quantitatively reducible with chlorostannous acid to the molybdenum blue complex.

A theoretical consideration of the molybdenum blue complexes (*4*, *7*, *17*) reveals that reduction of molybdates yields unstable blue reduction complexes, the color being destroyed on changing the acidity. Silicates react with molybdates under suitable conditions to form a yellow color due to the formation of a complex of the composition $H_4[Si(Mo_3O_{10})_4].nH_2O$. This complex is more sensitive to the action of reducing agents and more stable than the reduction complex from the molybdates.

The proper adjustment of the ammonium molybdate–acid-silica ratios was investigated. Too great an excess of silicate formed a deep yellow color which interfered with the colorimetric determination of tin.

Difficulty was experienced in duplicating the intensity of blue color when identical concentrations of tin were determined, owing to the rapid rate of oxidation of the reduced tin. After a number of methods were tried, including the use of inert carbon dioxide atmosphere, it was found that accurate, duplicable results could be obtained by pouring the silicomolybdate reagent directly into the solution containing the tin after the reduction period, while still in contact with the zinc, and decanting immediately. This procedure excludes the use of zinc dust. Best results were obtained by the use of zinc shot.

The next step in the operation is the separation of tin from various materials preparatory to the colorimetric determination; a distillation procedure proved most rapid and efficient. In the procedure of dissolution most of the arsenic will be removed. The only contaminating substance that may distill over is antimony. Nitric acid must not be present, since it will interfere in the colorimetric determination of the distillate. Numerous experiments were conducted to determine the exact conditions of temperature and distillation rate and the concentrations of reagents to effect the complete, uncontaminated separation of tin.

REAGENTS

Chlorostannous Acid Solution, 0.05 mg. of tin per ml. Dissolve 0.1 gram of pure tin in 100 ml. of 1 to 1 hydrochloric acid and dilute to 2 liters with 1 to 1 hydrochloric acid.

Silicate Solution, 1 mg. of silica per ml. Fuse 1 gram of pure silica with 5 grams of C.P. sodium carbonate, dissolve in distilled water, and dilute to 1 liter.

Molybdate Solution. Dissolve 5.3 grams of C.P. ammonium molybdate in 100 ml. of distilled water, add 10 ml. of concentrated sulfuric acid (specific gravity 1.84), and dilute to 200 ml.

Silicomolybdate Reagent. Dilute 10 ml. of the molybdate solution to approximately 800 ml., add 2.5 ml. of the silicate solution, and dilute to 1 liter. Mix thoroughly and allow to stand 0.5 hour before use. Prepare a fresh supply daily from the stock solution of molybdate and silicate.

Zinc Shot. Reagent grade, low in arsenic, lead, and iron, weighing 0.4 to 0.5 gram per shot.

PROCEDURE

In case of ferrous metals containing less than 0.05% tin, weigh accurately a 10-gram sample for analysis; for metals higher in tin, use a proportionally smaller sample. Introduce the sample into a 250-ml. Claisen flask and add 200 ml. of a solution containing 15 ml. of concentrated sulfuric acid (specific gravity 1.84) and 30 ml. of concentrated hydrochloric acid (specific gravity 1.19). Add glass beads to minimize bumping. Evaporate to the first fumes of sulfuric acid, or until the residue is semisolid, but not to dryness. In case of nonferrous metals containing more than 0.05% tin, dissolve 1 gram of sample in a 400-ml. tall-form beaker with 15 ml. of concentrated sulfuric acid, 10 ml. of concentrated nitric acid (specific gravity 1.42), and 25 ml. of water. Fume strongly to remove excess nitric acid, transfer to a 250-ml. Claisen flask, and wash the beaker with 1 to 1 hydrochloric acid. Add glass beads and dehydrate.

After dissolution and dehydration of the sample, add 10 ml. of concentrated sulfuric acid. Place a 200° C. thermometer in the main neck of the Claisen flask with the thermometer bulb close to the bottom of the flask. In the other neck place a 50-ml. separatory funnel. Attach the side arm to a water condenser. Receive the distillate in a 100-ml. Erlenmeyer flask. A trap and caustic solution may be connected to the Erlenmeyer flask to prevent the escape of uncondensed hydrochloric acid vapors. Pour 10 ml. of concentrated hydrochloric acid and 15 ml. of 40% potassium bromide into the Claisen flask through the separatory funnel to prevent loss of tin. Transfer 40 ml. of concentrated hydrochloric acid to the separatory funnel. Distill the solution until the temperature of the solution in the flask reaches 138° to 143° C. Add the 40 ml. of concentrated hydrochloric acid drop by drop from the separatory funnel, keeping the temperature between 138° and 143° C. After all the acid has been added, continue distillation until the temperature rises to 150° C. Discontinue heating, disconnect the condenser, and wash it with 1 to 1 hydrochloric acid, collecting the washings in the flask containing the distillate.

The distillate now contains the tin, and requires only evaporation to a definite volume before being ready for the colorimetric determination.

The volume to which the distillate is evaporated before testing depends on the milligrams of tin present. Two procedures have been developed, depending on the concentration of tin.

MICROPROCEDURE (tin range 0.02 to 0.2 mg.). Evaporate the distillate to less than 6 ml., dilute to 6 ml. with 1 to 1 hydrochloric acid, and transfer to a 50-ml. Erlenmeyer flask. Heat to boiling, add 2 zinc shots, and shake while boiling for 1 minute. Pour 20 ml. of the silicomolybdate reagent into the reaction flask, mix, and decant immediately into a glass-stoppered Erlenmeyer flask, to separate the solution from the zinc within 10 seconds. Simultaneously run a standard containing 0.1 mg. of tin per 6 ml. by the same procedure. Compare the resulting blue colors after standing 5 minutes.

MACROPROCEDURE (tin range 0.2 to 1.0 mg.). Evaporate the distillate to about 25 ml., dilute to 30 ml. with 1 to 1 hydrochloric acid, and transfer to a 250-ml. tall-form Erlenmeyer flask. Heat to boiling, add 10 zinc shots (approximately 4 to 5 grams), and shake while boiling for 1 minute. Pour 100 ml. of the silicomolybdate reagent into the reaction flask, mix, and decant immediately into a glass-stoppered Erlenmeyer to separate the solution from the zinc within 10 seconds. Simultaneously run a standard containing 0.5 mg. of tin per 30 ml. of solution by the same procedure. Compare the resulting colors after standing 5 minutes.

No color is found in a solution containing no tin when the 10-second maximum mixing and decanting time is not exceeded. This period of time is more than ample to permit efficient operation.

RANGE OF CONCENTRATION AND CONFORMITY TO BEER'S LAW

A number of determinations were run on tin standards containing 0.02 to 1.5 mg. of tin. Solutions containing 0.18 mg. of tin or less were determined by the micromethod and above 0.18 mg. of tin by the macromethod. Each result was checked on both the photoelectric filter photometer (Fisher) and a Duboscq comparator, using 0.5 mg. of tin per 30 ml. as the standard. It is evident from Table I that excellent results, conforming to Beer's law, can be obtained for solutions containing up to a maximum of 1 mg. of tin. Concentrations of tin greater than 1 mg. per 30 ml. of 1 to 1 hydrochloric acid solution gave weaker color intensities than is required by the Beer's law straight-line relationship. In the micromethod a maximum error of 15% was found in the range from 0.02 to 0.2 mg. of tin, which represents an error of only 0.03 mg. of tin when 0.2 mg. is present. The macroprocedure as outlined will determine accurately within 5% of the actual value from 0.2 to 1 mg. of tin per 30 ml. of solution.

In all the determinations by both methods, the per cent of tin calculated from a reading with the Duboscq comparator closely checked the results obtained using the Fisher photoelectric filter photometer.

STABILITY OF REAGENT AND MOLYBDENUM BLUE COLOR

Experiments on the effect of aging of the silicomolybdate reagent disclosed that the freshly prepared reagent did not give satisfactory results if used immediately. After 24 hours, poor results were again obtained because of the decomposition of the heteropoly complex. Therefore, solutions were prepared each morning, or prior to use, allowed to react for 0.5 hour, and any excess was discarded at the end of the day.

The stabilities of the molybdenum blue complexes formed on reducing the silicomolybdate reagent with amounts of tin varying from 0.1 to 1 mg. per 30 ml. of 1 to 1 hydrochloric acid solution were determined by measuring the color intensities on the photometer at various intervals of time. Maximum color intensities are formed in each case within 5 minutes after reduction. For concentrations of tin equal to 0.6 mg. or less, only slight fading occurred in 1 hour. In greater quantities, fading is appreciable in 30 minutes. Readings taken after 5 minutes gave satisfactory results in all cases.

EFFECT OF ACIDITY

The acid concentration of the silicomolybdate reagent was varied so as to obtain a final normality of the mixture of reagent and tin solution containing 0.5 mg. of tin ranging from 0.82 to 1.72. Photometer readings at the end of 5 and 60 minutes showed that this wide range of normalities had slight effect on the development or stability of the blue color.

EFFECT OF DIVERSE IONS

A study was made of the effect of diverse ions that may be found in the distillate after separation of tin, as described in the procedure upon the blue color. Arsenic has little effect on the color until 5 mg. are present in the 30-ml. aliquot. Antimony interference is slight up to 3 mg. in the 30-ml. aliquot. These concentrations are very high and, therefore, no interference is to be expected in the majority of cases in which small quantities of tin will be determined. Concentrations of iron over 0.2 mg. per 30 ml. depress the color and give a greenish cast to the solution. The method of separation of tin used in the procedure excludes all but traces of these impurities and, therefore, little interference from them is found in an actual determination. In the absence of tin, the presence of antimony may lead to the determination of 0.1 mg. of tin per 30 ml.

RESULTS

Results of determinations on standard samples prepared by adding known quantities of tin to 10 grams of tin-free steel showed a maximum error of 4%. Table II shows the results of 45 determinations of National Bureau of Standards and Norfolk Navy Yard steel samples. The maximum deviation is 0.0018% and the maximum per cent deviation 0.0012. Also listed are 26 tin determinations of nonferrous metals. The maximum deviation is 0.023% tin and the maximum per cent deviation is 0.015 in manganese bronzes containing 0.2 to 0.5% tin.

Table II. Determination of Tin

Sample	No. of Detns.	Tin Found %	Deviation %
N.B.S. 25 Si steel[a]	4	0.0063	±0.0005
Steel from Norfolk Navy Yard	6	0.0065	±0.0012
N.B.S. 106, Cr-Mo-Al steel	4	0.014	±0.0005
N.B.S. 73 stainless steel	4	0.0029	±0.0002
N.B.S. 55 ingot steel	7	0.0029	±0.0002
N.B.S. 9C-Bessemer steel	5	0.0015	±0.0001
N.B.S.[b] 33-3% Ni steel	4	0.0039	±0.0002
N.B.S. 72B, Cr-Mo steel	5	0.0073	±0.0009
N.B.S. 126-36% Ni steel	6	0.0168	±0.0008
Mn bronze 133040	9	0.202	±0.005
Mn bronze 133041[c]	5	0.223	±0.015
Mn bronze 133042	6	0.390	±0.013
Mn bronze 133143[d]	6	0.415	±0.008

[a] Bureau of Standards analysis of tin = 0.007% includes any As or Sb.
[b] Determinations by micromethod.
[c] Gravimetric determination = 0.20% tin.
[d] Gravimetric determination = 0.43% tin.

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THE views presented in this article are those of the writers and are not to be construed as the official views of the Navy Department.

Hallett Appointed Associate Editor

Chapman, Churchill, and Oser Elected to Advisory Board

It is with a deep feeling of satisfaction and personal pleasure that I announce the appointment of L. T. Hallett as associate editor of the ANALYTICAL EDITION of INDUSTRIAL AND ENGINEERING CHEMISTRY, and report the election by the Council of R. P. Chapman, J. Raynor Churchill, and Bernard L. Oser to the Advisory Board.

Dr. Hallett brings to the publication a wealth of diversified experience in the analytical field. He will devote a considerable portion of his efforts to initiating new editorial programs.

The Advisory Board of the ANALYTICAL EDITION has been functioning very actively now for slightly more than a year. The members of the board and your editor have felt that several highly important specialized divisions of analytical chemistry were not satisfactorily represented by the existing make-up of the membership of the board. Accordingly permission was requested to increase the membership from six to nine. At the most recent meeting of the board, held in Washington, January 22, 1944, the question of what fields should be more directly represented at this time was analyzed and nominations by members of the board were carefully considered. The names of Messrs. Chapman, Churchill, and Oser were presented by the editor to the Council at its meeting in Cleveland, April 5, 1944. I am happy to state that these individuals were unanimously elected.

Walter J. Murphy

Lawrence T. Hallett brings to his position as associate editor of the ANALYTICAL EDITION a background in analytical chemistry dating from his associating while an undergraduate at the University of British Columbia with E. H. Archibald, professor of chemistry, who had been a student of T. W. Richards. This early interest in precise analytical methods was deepened while working on a master's thesis on preparation of pure rubidium and cesium chloroplatinates and determination of their solubilities. In fulfillment of his mother's wish that some part of his education be obtained in the United States, he undertook further graduate study in analytical chemistry at the University of Wisconsin.

Lawrence T. Hallett

After a few months of instructing, a full-time graduate fellowship was taken in the development of microanalytical methods for the analysis of lake water residues. After receiving a Ph.D. from the University of Wisconsin in 1928, he had a brief excursion into teaching analytical chemistry at Oregon State College and research on thermal insulation.

In 1933 he joined the Eastman Kodak Company to develop a laboratory for microanalysis and thereby found his long cherished opportunity to prove that micromethods were both accurate and rapid and entirely suited to use in industry. After establishing the laboratory, he became interested in organizing the company's various analytical departments, both plant and research, into a coordinated group. This was effected by holding conferences for the demonstration and application of the newer instrumental methods to analytical problems in research and plant control. While at Eastman, apparatus for automatic microcombustions was designed and perfected.

An opportunity to pursue further the path started at Eastman came with the organization of a Research Laboratory at Easton, Pa., by General Aniline and Film Corporation. Early in 1943 he was given the responsibility of organizing the analytical chemistry of the new laboratory and now is actively engaged in developing and applying the newer techniques of microchemistry and instrumental methods to the research and plant problems of this company.

Dr. Hallett was born November 7, 1900, in Oakland, Calif., and received his B.A. in 1923 from the University of British Columbia. He was secretary of the Microchemical Section of the AMERICAN CHEMICAL SOCIETY in 1937, chairman in 1939, and served on several analytical committees during the intervening years. Publications include articles on solubilities, microtechniques, and review on organic microchemistry. He contributed the section on microanalysis in Scott's "Standard Methods of Chemical Analysis".

Ray Parkin Chapman, in charge of the central analytical laboratory in the Stamford Research Laboratories, American Cyanamid Company, was born in the Province of Prince Edward Island, Canada, July 15, 1898. He received his A.B. degree from Mount Allison University, Sackvilla, New Brunswick, Canada, in 1921, after having taken time out from college for two years' service with the Canadian Expeditionary Force of World War I. He taught chemistry and mathematics in high school for several years, meanwhile attending summer sessions at Columbia University (Teachers College) and receiving his M.A. degree in 1928. He entered Columbia University as a graduate student in the Department of Chemistry in 1929 and received his Ph.D. degree in 1932, serving during this period first as assistant in chemistry at Columbia and later as instructor at St. Stephen's College. His research for the doctorate dealt with indicators for oxidation-reduction reactions and resulted in the discovery of the indicator properties of the now familiar ferrous o-phenanthroline complex ion.

After a year as research assistant at Columbia he joined the Experimental Laboratory of the American Cyanamid Company at Linden, N. J., in 1933. He has been in charge of the central analytical laboratory of that company's Stamford Research Laboratories since its organization in 1937.

He has been a member of the AMERICAN CHEMICAL SOCIETY since 1931, and is a member also of various committees of the American Society for Testing Materials and of Sigma Xi and Phi Lambda Upsilon.

J. Raynor Churchill was born in Denver, Colo., in 1911 and went to Pittsburgh in 1919, when his father, H. V. Churchill, became chief chemist of the Aluminum Company of America. Intending to become a mechanical engineer, he worked for a few months in the Machine Shops of the Aluminum Company of America, and for a year as a millwright at the Ford Plant in Detroit. Returning to Pittsburgh, he entered the Evening College of Engineering at the Carnegie Institute of Technology. In 1929 he joined the staff of the Aluminum Research Laboratories as laboratory assistant. He completed the 9-year evening

J. Raynor Churchill

Ray P. Chapman

SHELBURNE STUDIOS

Bernard L. Oser

course at Carnegie Tech in 1938, obtaining the bachelor's degree, and took a number of graduate subjects in the evening school during the next few years.

Most of his professional experience has been in the field of spectrography from the time the first modern spectrograph was obtained by the Aluminum Company of America in 1931. He became chief spectrographer in 1941 and has been in charge of the company's spectrographic operations since that time. He has had an important part in the tremendous expansion of its analytical facilities during the past few years. The company is now carrying on the bulk of its metallurgical analysis by means of the spectrograph and is using 40 spectrographs in 31 laboratories distributed over the country. Most of his time during the past few years has been spent on the development of equipment and techniques for spectrographic analysis and in the technical supervision of spectrographic laboratories. He has done some research in allied fields and has been the author or co-author of papers on spectrography, electrographic methods of analysis, and corrosion phenomena.

Bernard L. Oser was born in Philadelphia, February 2, 1899. He received the B.S. in chemistry from the University of Pennsylvania in 1920, working under Edgar Fahs Smith, and the M.S. in 1925, working under D. Wright Wilson; and his Ph.D. in 1927 from Fordham University, working under Carl P. Sherwin.

He was employed as chemist in the Dermatological Research Laboratories from 1918 to 1920, as assistant in the Department of Physiological Chemistry, Jefferson Medical College, from 1920 to 1922, and as instructor in the Department of Chemistry, Graduate School of Medicine, University of Pennsylvania, and biochemist, Philadelphia General Hospital, from 1922 to 1926. In 1926 he joined Philip B. Hawk as assistant director in charge of the biological laboratories of the Food Research Laboratories, Inc.; in 1934 he became director and in 1939 vice president.

He has been a collaborator on all revisions of Hawk and Bergeim's "Practical Physiological Chemistry" since the 8th edition and author of several chapters, including those on blood chemistry and vitamins and deficiency diseases. He is the author or co-author of numerous scientific papers relating principally to vitamin methodology, stabilization, and control in foods, fish liver oils, and pharmaceutical products.

He has been a member of the American Chemical Society since 1927, and is at present a member of the Executive Committee, Division of Agricultural and Food Chemistry. Memberships in other scientific societies include: American Association for the Advancement of Science, American Institute of Chemists, New York Academy of Science, Institute of Food Technologists, Animal Vitamin Research Council, Association of Consulting Chemists and Chemical Engineers, Committee on Valid Certification of the American Standards Association, and American Association of Scientific Workers.

Standard Samples of Hydrocarbons

Work was begun at the National Bureau of Standards on July 1, 1943, on the preparation of standard samples of hydrocarbons of known high purity for calibrating analytical instruments and apparatus in the research, development, and analytical laboratories of the petroleum, rubber, and allied industries. Only a limited quantity of each hydrocarbon has been prepared and the purity of each has been pushed only to a point that is believed to be amply adequate for the present urgent needs for calibration. Fifteen hydrocarbons are now available under this program (see table).

Compound	N.B.S. Standard Sample No.	Amount of Impurity, Mole Per Cent
n-Pentane	201	0.25 ± 0.10
2-Methylbutane (isopentane)	202	0.13 ± 0.06
n-Hexane	203	0.24 ± 0.09
2-Methylpentane	204	0.25 ± 0.10
3-Methylpentane	205	[a]
2,2-Dimethylbutane	206	0.12 ± 0.05
2,3-Dimethylbutane	207	0.06 ± 0.04
Methylcyclopentane	208	0.25 ± 0.09
Cyclohexane	209	0.012 ± 0.007
Benzene	210	0.05 ± 0.02
Methylbenzene (toluene)	211	0.04 ± 0.02
Ethylbenzene	212	0.20 ± 0.07
1,2-Dimethylbenzene (*o*-xylene)	213	0.14 ± 0.05
1,3-Dimethylbenzene (*m*-xylene)	214	0.17 ± 0.07
1,4-Dimethylbenzene (*p*-xylene)	215	0.07 ± 0.03

Designation to Follow Standard Sample No.	Volume of Hydrocarbon, Ml.	Kind of Container	Cost per Sample
−5	5	Plain ampoule, sealed in vacuo	$3.00
−85	8	Special ampoule, with internal vacuum break-off tip, sealed in vacuo	5.00
−25	25	Plain ampoule, sealed in vacuo	9.00

[a] Not determined; believed to be the same as for 2-methylpentane.

The cost includes delivery in the United States, Mexico, Canada, Cuba, and United States possessions. For other countries, 50 cents postage must be added for each container, plus 25 cents for insurance or registration of each shipment.

Payment must be made with order. Orders should be addressed to the National Bureau of Standards, Washington 25, D. C., specifying clearly by number and name the hydrocarbons and containers wanted.

Sensitive Indicator for Volumetric Determination of Boiler Feedwater Alkalinity

The reagents used in preparation of the indicator for volumetric determination of boiler feedwater alkalinity [Ind. Eng. Chem., Anal. Ed., 15, 742 (1943)] are:

1. Alphazurine, National Aniline Division, Allied Chemical & Dye Corp., reagent 205.
2. Methyl red sodium salt, Eastman organic chemicals, No. 1462.

Bureau of Ships
Navy Department
Washington, D. C.
Harry Fleisher

NOTES ON ANALYTICAL PROCEDURES

Textile Finishes and Fiber Identification Stains

BRAHAM NORWICK[1], Beaunit Mills, Cohoes, N. Y.

IT HAS been recognized that dye mixtures such as the Hahn stains and the more versatile Davis and Rynkiewicz modification (*1*) are not entirely adequate for the identification of treated rayon fibers likely to be encountered in processed fabrics. The presence of added substances in the yarn, as well as the chemical and physical history of the fabric, frequently results in peculiar alterations of test dyeing properties. Under such circumstances, once the yarns are known, anomalous dyeing may serve to determine the finish or the extent to which processing has been carried. When the treatment is known, the shade obtained may be of value in control, once one has established a set of standards; this is illustrated in Table I, which indicates the influence of causticizing upon subsequent test dyeing with the Davis and Rynkiewicz stain.

Table I. Effect of Caustic Treatment upon Subsequent Dyeing

	Concentration of Caustic				
	1%		5%		25%,
Time *Min.*	25° C.	50° C.	25° C.	50° C.	25° C.
			Acetate		
0.5	Greenish yellow	Greenish yellow	Greenish yellow	Green	Greenish yellow
1	Greenish yellow	Green	Greenish yellow	Green	Greenish yellow
5	Greenish yellow	Blue	Green		
			Viscose		
0.5	Lavender	Lavender	Blue	Violet	Dark blue
1	Lavender	Lavender	Blue	Violet	Dark blue
5	Lavender	Lavender	Violet	Dark blue	Dark blue

In testing samples which have had unknown treatment, one must first consider the primary color components which go to make up the shade obtained. The possible significance of the various colors is not easily limited, but the probabilities, especially when considered along with the particular type of fabric under examination, are indicated in Table II.

Table III indicates how one may make further subdivisions in such a typical treatment as sizing.

The various families of finishes may be distinguished by test dyeing before and after special treatments: enzymes for proteins, 5% sulfuric acid at a boil for urea-formaldehyde resins, alcoholic extraction for cationic softeners.

[1] Present address, Aberdeen Proving Ground, Md.

Table II. Color Components

Blue	Yellow	Red
Cuprammonium	Acetate	Viscose
Cotton	Nylon	Attacked wool
Vinyon	Wool	Aldehyde resins
Sizes	Heavy oiling	
Cationic materials	Melamine	
Attacked viscose	Aldehyde resins	
Attacked acetate		

Table III. Alkali- and Water-Soluble Sizes

Blue	No Color
Starches	Natural gums
Protein adhesives	Natural resins
Cellulose ethers	Alkyd resins
Polyvinyl alcohols	

The fibers based upon cellulose can be treated to give test dyeings in all the available shades.

Cotton, dried with formaldehyde and a trace of acid, moistened with ammonia, and then heated either in an oven or in an organic liquid such as lauryl alcohol, quickly loses its ability to pick up blue and shows first reddish shades and then yellows. Drying cotton with glyoxal gives similar results. The presence of melamine, even if unreacted—that is, in a state where it is extractable with water—as it might be if employed for inhibiting the gelatinizing action of concentrated sulfuric acid upon cotton, causes the latter to pick up yellow. Drying viscose with glyoxal yields a yarn which dyes a pale yellow. The common creaseproof and shrink-resisting urea-formaldehyde finish gives yellow shades: one interesting sample of plain-weave spun rayon showed a test dyeing yellow on one face and lavender on the other, due to the use of dry cans contacting and reacting the resin on only one face of the fabric.

Incomplete and uneven desizing, which may be manifested in a variety of ways, such as a slight uneven luster or dullness, or variable tear strengths and air permeabilities, can be rapidly detected on known fabrics of nylon, viscose, and acetate, since the common size materials stain a deep, contrasting blue. In such cases, and with mixed fibers, examination of the dyed sample under a low-power microscope may be a source of further information about the condition of the material.

There is a relation between the extent of alteration of test dyeing properties and the effective treatment, but this is generally true only over short ranges, and even there one will find in commercial treatments that interferences uncontrollable by the analyst are of such magnitude that in general only qualitative information can be obtained.

Appreciating this fact, however, for satisfactory qualitative tests, the analyst has considerable leeway, following the Davis and Rynkiewicz staining suggestions.

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Priority Assistance to Laboratories

Conditions under which priority assistance is given to laboratories were clarified March 6 by the issuance of Preference Rating Order P-43 as amended. Any person who carries on scientific or technological investigation, testing, development, or experimentation in his business is considered to operate a laboratory in buying material for these purposes, even though he does not have a separate department or organization for such activities.

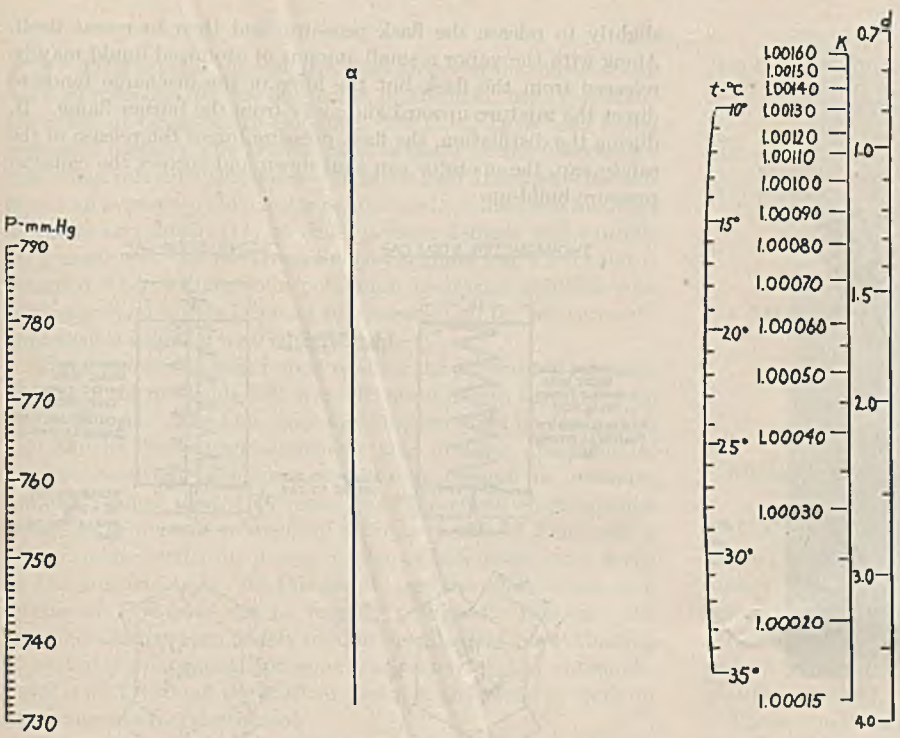
Priority ratings assigned by the order may be used to get materials for development of products designed primarily for future civilian markets only if such activities will be carried on without diverting any manpower, technical skill, or facilities from war work. Laboratories may not use AA-1 preference rating for activities connected with future civilian needs.

Restrictions on the quantity of aluminum that may be obtained under the order are removed.

Priorities assistance assigned under P-43 may be used for construction jobs costing not more than $500 without applying for permission to start construction under L-41. Procedure for obtaining controlled materials has been simplified, and the allotment number V-9 is used in place of MRO-P-43.

Nomographic Chart for Correcting Weights to Vacuum

HENRY C. THACHER, JR., C.W.S. Development Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.



ALTHOUGH the correction of weights in air to in vacuo is a very common operation in many fields of precise work, the use of the tables available in handbooks is rather cumbersome when the correction must be applied frequently. Moreover, in many instances greater precision may be required than is obtained by using tables based on constant air density.

The correction factor, K, by which the air weight of an object must be multiplied to give its weight in vacuo is a function of the density of the object, the density of the weights used, and the density of the air. The density of the air, in turn, is a function of the barometric pressure, the temperature, and the relative humidity. The effects of pressure and temperature upon the density of the air are relatively great, while the influence of humidity is considerably less, diminishing the effective pressure by 0.3783 times the partial pressure of water vapor.

The accompanying nomograph facilitates the correction of weighings with brass weights to vacuum. All variables except relative humidity of air have been included within the limits indicated below. A constant relative humidity of 50% has been used.

Temperature, 10° to 35° C.
Barometric pressure, 730 to 790 mm. of mercury
Density of object, 0.7 to 4.0
Density of brass weights, 8.4

Inasmuch as the effect of humidity of the air is small, limited variations in relative humidity will have only a slight effect on results. The nomograph therefore offers a more rapid means of computing correction factors and at the same time permits a higher degree of precision, since it is based on constant air humidity rather than on constant air density.

In constructing the chart, it has been assumed that dry air obeys the ideal gas law, and that the effect of humidity upon air density is given by subtracting 0.3783 times the partial pressure of water vapor from the observed barometric pressure. Where d_a is the density of the air, d_m is the density of the object, and d_w is the density of the weights, the vacuum correction factor, K, is given by $K = d_m(d_w - d_a)/d_w(d_m - d_a)$. When d_a^2/d_m is negligible in comparison with d_m, this reduces to the commonly used equation, $K = 1 + d_a(1/d_m - 1/d_w)$, which has been used in the construction of this chart.

USE OF THE CHART. To use the chart, draw a line from the observed Centigrade temperature on scale t to the observed pressure on line P. From the intersection of this line with line α draw a second line to the density of the object on line d. Then factor K will be found at this second line on scale K, and the vacuum weight of the object may be obtained by multiplying the observed weight by this factor.

For example, suppose that an object of density 0.70 when weighed in air at 50% relative humidity, 770-mm. barometric pressure, and 20° C., weighs 100.000 grams. Then drawing a line connecting 770 mm. and 20° C., and a second line from 0.70 on the d scale to the intersection of the first line with the α scale, we find K equals 1.00158, and the vacuum weight of the object is 100.158.

Or again, when with an object of density 1.5 weighing 10.0000 grams in air at 50 per cent relative humidity with barometer reading 760 mm. and temperature 25° C., K is found to be 1.00064, the true weight of the object is 10.0064 grams.

The chart may be mounted on a piece of cardboard, and indexes made of loops of thread of suitable length with rubber bands or light springs to give sufficient elasticity. If such loops of thread are placed around the chart, they can be moved at will, and make it unnecessary to draw lines on the chart.

Joining Plastic Tubing to Glass

RICHARD KIESELBACH, Bakelite Corporation, Bound Brook, N. J.

BECAUSE of the present scarcity of rubber and copper, thermoplastic tubing is becoming increasingly popular for laboratory use. Where chemical inertness is desirable, it is far superior to the materials it replaces.

The conventional method of joining plastic tubing to glass involves the use of a short length of rubber tubing. This method is usually satisfactory, where a temporary joint is required. For more permanent connections, or where the use of rubber is objectionable, a neat, strong, vacuum-tight joint can be made in the following manner:

Draw out the end of the glass tubing to a gradual taper, cutting it off at the point where its outside diameter is slightly less than the inside diameter of the plastic tubing. Fire-polish the end and let cool. Then heat the tapered section uniformly in a Bunsen flame for about 2 seconds, and quickly force it into the end of the plastic tubing for a distance of at least 1 cm. (Care must be taken to avoid overheating the glass, since it will then char the plastic.) While it is still hot, press the curled end of the plastic tubing to the glass with the fingers, to give the joint a smoother appearance. Allow the joint to cool thoroughly before putting it into service.

A properly made joint of this kind will be found to be as leakproof as the tubing itself, and able to withstand a surprising amount of mechanical stress.

Safety Cap for Laboratory Glass Distillation Equipment

GEORGE A. RADER, Standard Oil Co. of California, Richmond, Calif.

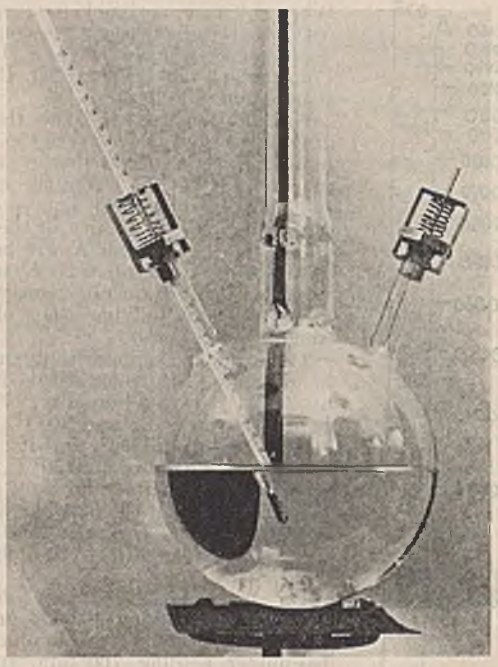


Figure 1

ONE common cause of damaging fires in petroleum laboratories is the accidental building up of excessive pressure in distillation flasks. Such flasks are usually equipped with two stems or necks, one used as the filling stem and the other for a thermometer. Both openings are ordinarily closed with a cork. During the distillation the reflux column or condenser may become plugged, there may be a sudden formation of foam, or the operator may neglect to open a vent line, thereby causing unusual pressure to build up in the flask. When this occurs one cork may be forced out, releasing an appreciable volume of flammable vapor plus liquid which flashes, and the result is a laboratory fire.

A safety device (Figures 1 and 2) has been developed for the purpose of preventing such fires. One device is attached to each stem and acts as a safety valve by permitting the cork to lift slightly to release the flask pressure, and then to reseat itself. Along with the vapor a small amount of atomized liquid may be released from the flask but the force of the discharge tends to direct the mixture upward and away from the burner flame. If, during the distillation, the flask pressure forces the release of the safety cap, the operator can shut down and correct the cause of pressure build-up.

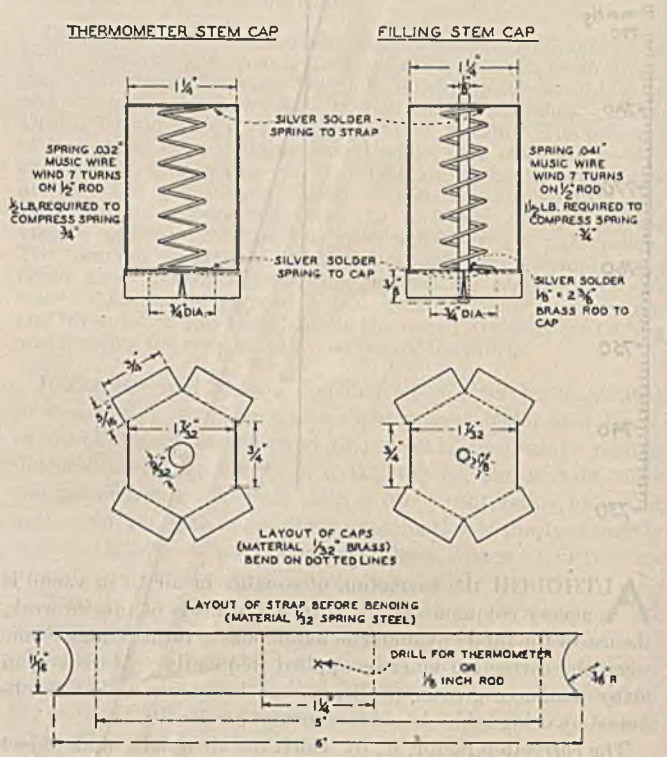


Figure 2

During the tests and demonstrations on laboratory distillation equipment, no flashes or fires resulted, but it is believed that under some conditions a flash is possible. The total amount of stock released, however, is generally so small that serious consequences are not likely to result.

Improvements in the Determination of Iron by the Nitroso R Salt Method

C. P. SIDERIS, H. Y. YOUNG, AND H. H. Q. CHUN, Pineapple Research Institute of Hawaii, Honolulu, T. H.

THE selection of a new light filter which is more sensitive to the color of the iron salt of 1-nitroso-2-hydroxy-3,6-naphthalene disodium sulfonate and the introduction of certain improvements in the nitroso R salt method for iron (*1*) have made necessary revision of the original procedure.

PROCEDURE. Add to a 10-ml. aliquot of the unknown in a 50-ml. Pyrex test tube, 0.5 ml. of 10% hydroxylamine sulfate and a drop of 0.05% metanil yellow (aqueous solution) and neutralize with 14% ammonium hydroxide drop by drop until a pinkish-yellow color is obtained. (If a decidedly yellow color is produced, add one drop of 6 *N* hydrochloric acid.) Then add to the mixture 1 ml. of 0.5% nitroso R salt and 2 ml. of 4 *N* sodium acetate and dilute to a definite volume, in the range of 20 ml. Determine color intensity in the photoelectric colorimeter from 2 to 24 hours later, using filter KS-66 with transmission limits of 640 to 700 millimicrons and a 2.5-mm. cell or a combination of a 10-mm. cell and a 7.5-mm. plunger as recommended for the Summerson-Klett photoelectric colorimeter. The 10-mm. cell is recommended for concentrations below 1 microgram per ml. A good linear relationship between concentration and colorimetric reading exists up to 10 micrograms of iron per milliliter.

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PUBLISHED with the approval of the Acting Director as Technical Paper No. 151 of the Pineapple Research Institute of Hawaii, University of Hawaii.

Some Color Tests for Rotenone Not Specific

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OF THE several colorimetric tests proposed for the detection of rotenone (*9*), the blue color, or Durham, test (*4*) and the red color, or Gross-Smith-Goodhue, test (*5, 6*) have been found especially useful. The Durham test is based on the observation that when rotenone is treated with nitric acid and then with ammonia an evanescent blue color is produced; it has been modified by Jones and Smith (*11*) to make it more delicate and suitable for general use. In the Gross-Smith-Goodhue test a red color is obtained when an alcoholic potassium hydroxide solution containing sodium nitrite is added to rotenone and the mixture subsequently is acidified with sulfuric acid.

Either test can be relied upon to show the presence of rotenone or some of the rotenoids (*13*) in specimens of *Derris*, *Lonchocarpus*, and *Tephrosia*. The blue color test has been used by Jones *et al.* (*10*) and by Sievers and associates (*14*) to select specimens of devil's-shoestring (*Tephrosia virginiana*) highest in rotenone content. Jones *et al.* (*10*) found that the effectiveness against houseflies of acetone extracts of various species of *Tephrosia* is well correlated with the degree of blue or blue-green color given by the Durham test. By this simple test the effectiveness of a sample of *Tephrosia* can be roughly predicted. Likewise, the red color test has been widely used in the quantitative evaluation of material containing rotenone and some of the rotenoids. Cahn *et al.* (*3*) found the method useful in an extensive study of the composition of derris root.

These color tests, however, are not always specific for rotenone in other genera of Leguminosae. For example, in 1937 Moore (*12*), searching for a domestic source of rotenone, reported its presence in *Amorpha fruticosa* because it gave a positive Durham test. Subsequently Featherly (*2*), of Oklahoma Agricultural and Mechanical College, confirmed the observations of Moore and proposed that seed of the plant be used as a source of rotenone during the war emergency. More recently, however, Acree, Jacobson, and Haller (*1*) have shown that rotenone is not present in the seeds of *A. fruticosa* and that the blue color is produced by a glycoside whose value as an insecticide remains to be determined.

The yam bean (*Pachyrhizus erosus*) also was reported to contain rotenone solely on the basis of the Durham test (*8*). Both this plant and *Amorpha fruticosa* give a positive red color test. Certain synthetic organic compounds have also been shown to produce an evanescent blue color when the Durham test is applied (*7*).

From the foregoing results it appears that considerable caution should be taken in interpreting the color obtained in both these tests when they are applied to plant material other than *Derris*, *Lonchocarpus*, and *Tephrosia*. Rotenone should be reported as present in plants only when it has been definitely isolated and characterized.

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Washing Selas Filtering Crucibles by Reverse Flow

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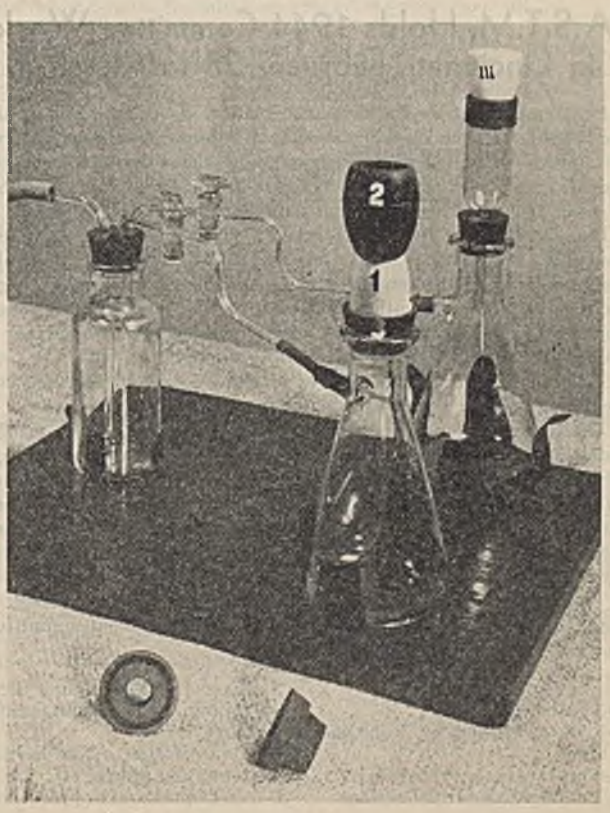
Michigan Agricultural Experiment Station, East Lansing, Mich.

SINCE it has become impossible to obtain asbestos for analytical filtrations as desirable as that formerly available, the author and his associates have sought equally effective and convenient means of quantitative filtration without the use of asbestos. Selas filtering crucibles meet these requirements for certain determinations, including potassium by the chloroplatinate method, sugar by use of Fehling's solution, and others.

These crucibles are similar to the Gooch type in shape but have a fixed, porous bottom for the filtering element, thereby eliminating the use of asbestos. Directions for cleaning recommend washing with hot water or hot acids by reverse flow in order to remove fine, insoluble particles lodged in the pores of the upper surface of the filter, but do not suggest a convenient, mechanical means of accomplishing this; hence, the author devised the ar-



rangement shown in the accompanying figure to facilitate the task.

1 is a Selas filtering crucible in position for being washed by reverse flow. 2 is a reservoir for the wash solution. It is arranged to fit tightly around the bottom of the crucible being washed and can be easily and quickly transferred from one crucible to another. This exchangeable reservoir was prepared from a large rubber pipet bulb by cutting off the top with a pair of shears and making a hole in the bottom with a cork borer. This hole must be of such size that the bulb can be slipped over the end of the crucible and will fit snugly enough to retain the wash liquid. Used bulbs, deteriorated at the point where they were stretched over glass tubing, may be utilized for such reservoirs, in keeping with the rubber economy program. A short length of Gooch rubber tubing would serve as a satisfactory substitute for such a bulb.

3, prepared from a No. 9 rubber stopper, holds the crucible safely in position for the effective application of suction. A circular groove in the top of the stopper accommodates the upper rim of the inverted crucible, and if filled with water before insertion of the crucible, it provides an effective seal against entrance of air when suction is applied. A large hole in the center of this holder permits exit of the wash liquid from the crucible into the suction flask. In order to use a stopper with a top larger than the mouth of these crucibles, it was necessary to reduce and taper the lower part to fit the neck of the suction flask. Front and side views of these holders are shown in the lower part of the picture. The hole in the center of the stopper was cut with a cork borer in the usual way; the groove in the top was made, and the lower part reduced, by use of a metal-cutting lathe.

These devices used in combination with the arrangement shown for holding the suction flasks and trap bottle provide a convenient means for washing Selas crucibles by reverse flow. After a crucible is washed several times in this way, it is placed in the ordinary crucible holder shown in the suction flask at the right for washing in the usual direction.

ACKNOWLEDGMENT

The author is indebted to Wm. Wallace, mechanic in the Department of Agricultural Engineering at Michigan State College, for operating the lathe in the preparation of a number of these crucible holders.

A.S.T.M. Holds 1944 Committee Week in Cincinnati, February 28 to March 4

In attendance at the 148 technical committee meetings held during the 1944 Committee Week in Cincinnati, February 28 through March 4, were 745 technologists, this figure being almost double that of the previous year, but the registration figure varies, depending on number of standing committees which participate in the group meetings.

Decision by the A.S.T.M. Executive Committee to issue its widely used Book of Standards in 1944 instead of 1945, the normal triennial year, led many of the committees to meet this year in March to get their specifications and other work as up to date as possible. Decision to advance the Book of Standards' publication by one year is caused by the unprecedented demand for the publication.

A number of major A.S.T.M. committees also held meetings immediately prior to or subsequent to Committee Week.

There are constantly increasing recognition and use of A.S.T.M. purchase specifications, methods of tests, and related standards. This is indicated by the demands for publications, the request from industry and government that technical committees extend their work into fields not covered, and also the organization of new committees, such as those on Adhesives, Metal Powders, and Aromatic Hydrocarbons.

The following main A.S.T.M. standing committees, except as noted, met in Cincinnati (usually there were numerous subcommittees and section meetings also):

A-1 on Steel
A-3 on Cast Iron
A-5 on Corrosion of Iron and Steel
A-6 on Magnetic Properties
A-7 on Malleable Iron Castings
A-10 on Iron-Chromium, Iron-Chromium Nickel, and Related Alloys
B-3 on Corrosion of Non-Ferrous Metals and Alloys
B-5 on Copper and Copper Alloys
B-6 on Die-Cast Metals and Alloys
B-7 on Light Metals and Alloys
B-8 on Electrodeposited Metallic Coatings
C-16 on Thermal Insulating Materials
D-1 on Paint, Varnish, and Related Products
D-2 on Petroleum Products and Lubricants
D-4 on Road and Paving Materials
D-5 on Coal and Coke
D-9 on Electrical Insulating Materials (Philadelphia, Pa., Feb. 21, 22)
D-11 on Rubber Products
D-17 on Naval Stores
D-20 on Plastics (Philadelphia, Pa., Feb. 23, 24)

NEW EQUIPMENT

Instrument for Measuring Small Particles

The Fisher sub-sieve sizer, for measuring the size of particles too small to be measured by sieves, is based on the apparatus described by Gooden and Smith [Ind. Eng. Chem., Anal. Ed., 12, 479 (1940)], and is made by Eimer & Amend, 635 Greenwich St., New York, N. Y. Operation has been simplified and a calculator chart provided to make operation easy. The instrument consists of an air pump, air-pressure regulating device, precision bore sample tube, double range flowmeter, calculator chart, and accessory equipment.

In operation, the motor-driven air pump builds up pressure in the pressure regulator to a constant head, so that a uniform flow of dry air passes through the packed powder sample and is measured by means of a double range flowmeter. The liquid level in the manometer varies with the air flow, depending on the resistance (particle size) of the particular sample. The average particle size of the sample in microns is read directly from the chart as indicated by the level of the fluid in the manometer. The range of the instrument is from 0.2 to 50 microns.

Capacitor for Electron Microscope

A 0.01-mfd. 40,000-volt direct current capacitor has been built for a special application of the electron microscope. It is capable of continuous operation at 80° C. and of withstanding total submersion and heavy surges. The case is welded steel measuring $4^{11}/_{16} \times 5^{3}/_{4} \times 7$ inches high with a standoff insulator 8.5 inches high, soldered directly to the case, thus eliminating the possibility of oil leakage or the entrance of moisture. It is manufactured by the Industrial Specialty Co., 1725 West North Ave., Chicago 22, Ill.

Lead Standard

The American Standards Association has announced approval of a new standard, Allowable Concentration of Lead and Certain Inorganic Compounds (Z37.11-1943), which sets safe limits for the amount of metallic lead, lead carbonate, lead sulfate, lead oxides, lead nitrate, and lead chloride allowable in the air of industrial workshops. It covers the physical and chemical properties of the substance, summarizes methods of test, and includes a comprehensive bibliography.

Copies may be obtained from the American Standards Association, 29 West 39th St., New York 18, N. Y., at 20 cents each.

BOOK REVIEWS

Semimicro Quantitative Organic Analysis. *E. P. Clark.* 1st ed. 135 pages. Academic Press, Inc., 125 East 23rd St., New York, N. Y., 1943. Price, $2.50.

The book was written for the purpose of providing laboratories, which are not equipped for precision microanalysis, with directions for analysis on a semimicro scale with samples ranging from 10 to 25 mg. It is excellent in this respect and fills a great need. However, the book fails to give a reasonable number of alternative methods or even a bibliography of such, and includes very few references to the literature dealing with the methods recommended. The author tries to justify this condition by stating in the preface that he did not attempt "to compile a reference book but rather to present in as brief a manner as possible simple working, well tested methods, which can be followed to a successful conclusion". Procedures are described which make use of microchemical apparatus, but it is unfortunate that the author, in his setups, has ignored the specifications of the American Chemical Society Committee on Standardization of Microchemical Apparatus, since all large glass blowers and scientific houses now have these. In many cases the apparatus described practically meets the specifications but they should have been complied with throughout. The reader will do well to use standard parts for all setups, except for the semimicroazotometer, which is much larger.

The book is divided into 13 chapters. Unfortunately, determinations of ash and metals have not been included.

Chapter I. Introduction. The use of a semimicrobalance is recommended and a table is included showing the relationship between the precision of a balance and the practical size of a sample to be weighed. At the top of page 3 the essential difference between precision and sensitivity does not seem to be appreciated. Temperature effects, lighting arrangements, care of the balance, calibration of the weights, and weighing are discussed, with directions for making various standard volumetric solutions for semimicro work. Filtering and drying apparatus are described and there are directions for determination of melting and boiling points. Some space is devoted to calculation of empirical formulas from analytical data.

Chapter II. Determination of Carbon and Hydrogen. The procedure is essentially the Pregl setup using micro-sized equipment. Lead chromate has been omitted from the standard tube filling and a preheater is employed. Approximately 10-mg. samples are burned in an atmosphere of oxygen at a temperature of about 550° C. for all samples. Persons using this book as a guide for their carbon-hydrogen determinations will do well to increase the temperature of their furnaces to about 680° C., as 550° C. is much too low for many classes of compounds. The author does not recommend a second combustion, which is also a rather dangerous procedure since many compounds have a tendency to sublime back; the author attempts to prevent this by the use of a platinum baffle. The specifications for the preheater, bubble counter, combustion tubes, absorption tubes, and Mariotte flask are not standard.

Chapter III. Determination of Nitrogen by the Kjeldahl Method. The author greatly favors the Kjeldahl method over the Dumas for practically all types of compounds, stating that only in the case of certain semicarbazones is the method not applicable. Included in his discussion is the Friedrich method for handling compounds containing N-N, NO, and NO_2. Diagrams for constructing an electric digester and the Parnass-Wagner electrically heated distillation apparatus are included.

Chapter IV. Dumas Method for Determination of Nitrogen. A semimicro setup is described which uses microcombustion tubes, and an azotometer of 5-cc. capacity constructed from a microburet. There is no three-way stopcock or other form of regulator between the combustion tube and the azotometer. Several carbon dioxide generators are described which give a good grade of gas. The author suggests that combustions here be done at a "dull red heat" and merely employs one combustion. It would be far better to use a temperature of about 650° to 680° C. and give the tube a second combustion following the procedure of Pregl.

Chapter V. Determination of Halogens. The ethanolamine-sodium method is presented as the one of greatest importance; following this is a description of the Carius method using 25-mg. samples with details for constructing the semimicro Carius furnace. Next is a description of the sodium peroxide fusion method, giving details for both gravimetric and volumetric procedures. The fusion mixture described on page 58 should not be prepared and kept as suggested, because of its explosive nature. For determination of iodine the Liepert volumetric method is stressed, and finally a method for displacing aliphatic iodine with bromine followed by titration of the iodine formed. The filter tubes are not standard. The catalytic combustion method for halogens should have been included.

Chapter VI. Determination of Sulfur. The author describes the Carius determination using 25-mg. samples and heating the bomb tubes to 300° C. This temperature is in disagreement with that recommended by the standard texts on microchemistry, which advise keeping the temperature below 270° C. because of the danger of fusion of barium sulfate in the glass. The analyst will do well to use the lower temperatures. The method described for filtering is not micro in nature but rather macro, since it suggests transferring the barium sulfate to a Gooch crucible with the aid of a stirring rod. The reader will do well to use the methods generally employed for microdetermination of sulfur, either the inverted filter method or the Neubauer crucible. As in the chapter on halogens, the catalytic combustion method should have been included.

Chapter VII. Determination of Phosphorus. The alkali-nitrate fusion method for converting organic phosphorus to orthophosphate, followed by conversion of phosphorus to phosphomolybdic anhydride according to Woy's procedure, is given. The Kjeldahl and sodium peroxide methods are mentioned but not recommended, although they are known to give excellent results.

Chapter VIII. Determination of Methoxyl and Ethoxyl Groups. A semimicro alkoxyl apparatus is described and a slightly modified Viebock and Schwappach volumetric procedure used. The setup is certain to give low results with such compounds as methyl esters, which split off methyl alcohol almost immediately upon contact with the hydriodic acid, unless the reaction mixture is allowed to stand at room temperature for about a half an hour before heating of the hydriodic acid is begun. The analyst would do well to modify the setup to include a reflux condenser between the boiling flask and the trap, while the latter should contain sodium thiosulfate and cadmium sulfate in place of water, as the author recommends. Valuable information is given regarding the preparation of acid suitable for the determination, as even the so-called reagent grade of hydriodic acid recommended for microanalysis gives tremendous blanks.

Chapter IX. Determination of Acetyl Groups. The author recommends hydrolysis of the acetyl compounds with ethanolic or *N*-butanolic potassium hydroxide for *O*-acetyl or *N*-acetyl compounds respectively, followed by acidification, distillation, and titration of the liberated acetic acids. This method was chosen in preference to the very excellent one of hydrolysis with *p*-toluene sulfonic acid followed by vacuum distillation of the acetic acid. The reader will do well to use the latter method of Elek and Harte or at least read the earlier articles by Clark, referred to in the footnotes, before trying his method.

Chapter X. Determination of the Neutralization Equivalent. A procedure for determining the neutralization equivalent of compounds is given, together with some valuable suggestions in the so-called notes.

Chapter XI. Determination of Molecular Weights. The Signer method of isothermal distillation and the Rast method of freezing point lowering are presented, with greater emphasis upon the former method. The author describes an apparatus for use with the isothermal distillation method. No reference is made to the work of Niederl and his collaborators which the reader will do well to review.

Chapter XII. Determination of Volatile Fatty Acids. The author describes in detail a method for qualitatively and quantitatively determining volatile fatty acids in dilute solutions, chiefly based on his own work. Examples are given as to the usefulness of this method. The earlier papers referred to in the footnotes should be read before attempting this work.

Chapter XIII. Some Useful Tables. There are included tables of gravimetric factors, barometer corrections for temperature, atomic and molecular formulas and some of their multiples, the carbon and hydrogen percentages and molecular weights of a series of CHO compounds from C_{16} to C_{32} frequently encountered among natural products and their derivatives, and a five-place table of logarithms of numbers from 1 to 10,000. A rather complete index follows at the end.

Al Steyermark

Laboratory Manual of Spot Tests. *Fritz Feigl.* Translated from German manuscript by *Ralph E. Oesper.* 276 pages. Academic Press, Inc., 125 East 23rd St., New York 10, N. Y., 1943. Price, $3.90.

This book was consciously designed by its author for the teaching of advanced chemistry in general, and of spot-test analysis in particular. The reviewer deliberately lists advanced chemistry as the subject of primary pedagogical interest, despite the book's title. Thus are marked two departures for Professor Feigl: whereas his former works were monographs for the laboratory worker in the specialized field of spot analysis, this volume is intended primarily for the student who is learning, not spot testing or even analysis, but advanced chemistry in general.

This is an interesting idea. The author's argument points out that college courses in classical qualitative analysis are offered not so much for the purpose of producing chemical analysts, but as a framework, interesting and useful in itself, on which to hang much of the body of fact and theory that constitutes the essentials of chemical science. The argument submits simply that spot testing itself is sufficiently broad in its foundations, and tortuous in its ramifications into the bases of chemistry, to justify its use as a similar framework. The reviewer is not a teacher, and must leave to teachers the authoritative judgment on the validity of this argument; but he hopes that Feigl's unique idea, and this excellent book that is its medium, will be accorded their sympathetic attention. "Extremely important teaching goals", the author writes, "are: the closest possible correlation between handiwork (*sic*) and knowledge; the development of a critical sense; the acquisition of the ability to discern the relations of individual observations and findings to each other." If this book facilitates the achievement of these goals, its worth will have been demonstrated.

The reviewer need add nothing to the author's summary of the book's contents:

The Manual opens with a general discussion of the theoretical foundations of the subject. Then follows a chapter on the technique of spot testing, including a description of the necessary equipment. Next comes a chapter, in six parts, giving an extended treatment of surface and capillary effects, which are of such great importance in spot reactions. Appropriate instructive experiments are described. The following chapter deals with spot reactions designed to detect or identify inorganic materials. . . . The next chapter, on Qualitative Organic Spot Analyses, consists of three parts: detection of certain elements in organic compounds, detection of certain characteristic groups of atoms, detection of certain compounds. This arrangement accords best with the fundamentally different types of problems encountered in qualitative organic analysis. The three succeeding chapters deal respectively with the practical application of spot reactions to the testing of rocks and minerals, industrial materials, biological substances. Numerous practical examples are given in each of these chapters. The Manual closes with a chapter on Quantitative Determinations by Means of Spot Colorimetry.

Much of the material in this book will of course be found, differently presented, in the author's previously published "Spot Tests"; but there is a considerable amount of new material, too. The reviewer is particularly pleased to see the inclusion of the three chapters on the practical testing of rocks and minerals, industrial materials, and biological substances.

The book has an attractive appearance. No typographical errors were noticed.

BEVERLY L. CLARKE

Examination of Waters and Water Supplies. *Ernest Victor Suckling.* 5th ed. 849 pages. Blakiston's Son & Co., Philadelphia, Pa. Price, $12.00.

This is the latest edition of the original text which was first issued by J. C. Thresh in 1904 and has been a standard textbook on water supplies and their examination since that time. The present edition is of broader scope than the fourth, published in 1933, and contains valuable information on water treatment, primarily from a sanitary viewpoint.

This revised, expanded, and modernized text is divided into eight parts, with several chapters under each section. The arrangement and selection of the material are excellent and, like the former editions, the book is very well written. The subject is presented largely from the viewpoint of British requirements, but the author has referred to recent practices in this country and has drawn extensively from articles and papers in technical journals and similar publications in the United States. These references have been selected with care and will be helpful to those wishing to refer to the origin of a great deal of the data presented. The book will be found informative to scientists in this country who are interested in certain phases of water-borne diseases, since there is much material in it which is not readily available in American texts.

The analytical data and illustrations, especially those relating to microscopic organisms, have been very well prepared. The book will be a valuable addition to any sanitarian's library, and its purchase is especially justified as a reference work.

S. T. POWELL

Standard Methods for Testing Petroleum and Its Products. 5th ed. 500 pages, 127 diagrams. Institute of Petroleum, London, England, and American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa., 1944. Price, $3.00.

This new edition of The Institute of Petroleum's handbook contains details of 97 methods for testing petroleum and its products.

New matter includes an additional method for determining aniline points of volatile materials, a low-temperature filtration test for gas oil and Diesel fuels, the Fraass breaking point test for bitumen, a congealing point test for waxes for which the setting point method is unsuitable, a method for determining the water tolerance of a motor fuel, new distillation tests for crude oil and residues, a method for estimating the salt content of crude oil, and the use of the Abel flash point apparatus for viscous petroleum mixtures and of the N.G.A.A. metal pycnometer for determining the specific gravity of liquefied gases. A.S.T.M. methods, with slight modification, have been adopted for determining the tetraethyllead content of motor fuel and the residue on evaporation of kerosene and tractor fuels.

An innovation is inclusion of methods for testing bituminous emulsions and chemicals derived from petroleum. The sampling methods have been completely revised, and major alterations have been made in methods for acidity, ash content, Ramsbottom carbon residue, cold test of motor fuels, color (Lovibond), dielectric strength, doctor test, drop point, free acid and alkali in grease, knock rating, oxidation of lubricating oils, oxidation (gum) stability of motor fuels, penetration, sludging value, softening point, Reid vapor pressure, and kinematic viscosity.

Specifications for wartime hydrometers and thermometers are included, and the Appendix has been enlarged by the addition of a standard scheme for evaluating crude oils and a vapor pressure/temperature nomograph for hydrocarbons.

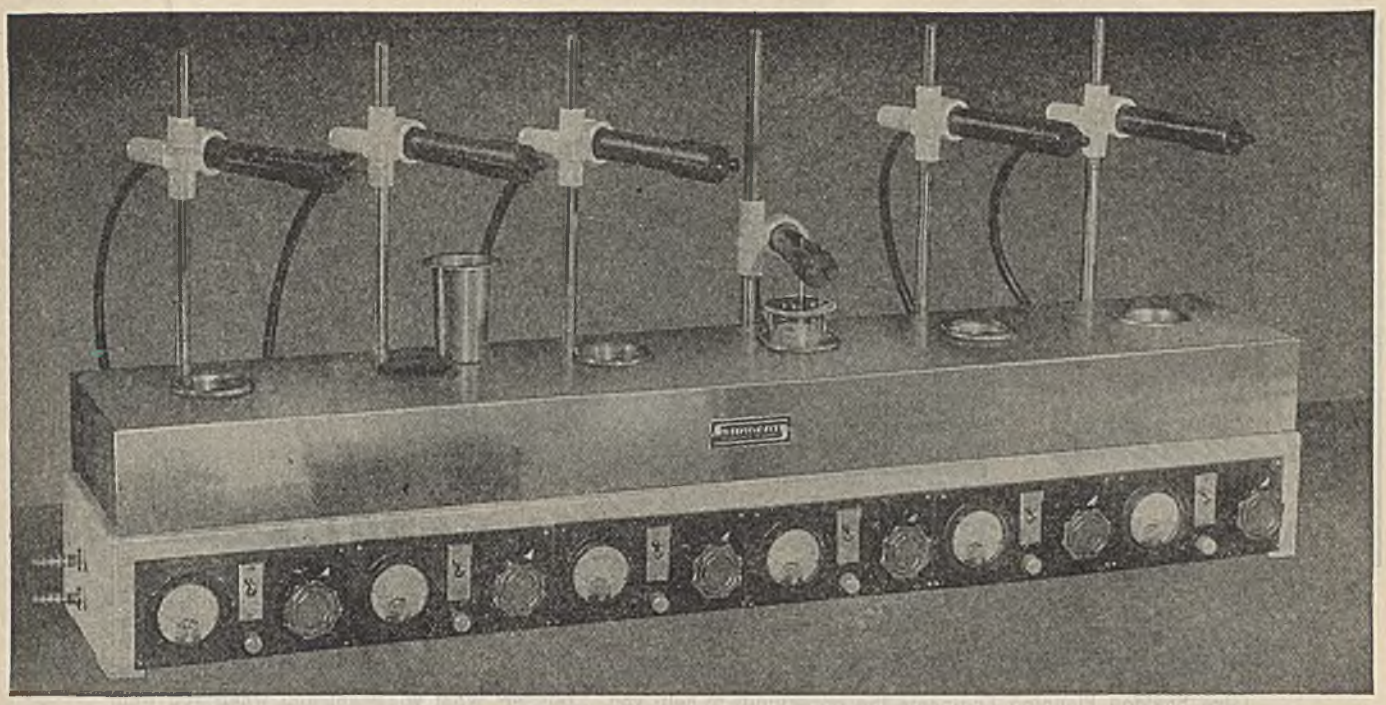
Directory of Textile Testing Laboratories

The Directory of Commercial and Educational Textile Testing Laboratories is being released by the Textile Foundation at this time when test methods and specification requirements are all-important to manufacturers and consumers. Laboratories are listed alphabetically, according to tests which they are equipped to perform, and geographically, in a 20-page pamphlet.

The foundation is particularly anxious to make available a complete and up-to-date directory and would welcome the names of textile testing laboratories not listed, as well as suggestions which would make a revised directory of greater value. Single copies are sold for 25 cents, 5 for $1.00, by the Textile Foundation, Industrial Building, National Bureau of Standards, Washington 25, D. C.

Analysis of Coal and Coke

The American Standards Association recently announced approval of a revision of the Standards Methods of Laboratory Sampling and Analysis of Coal and Coke (K18.1-1944), the work of Committee D-5 of the American Society for Testing Materials. The standard has been widely used since it was adopted in 1927, and has been revised several times previously. It may be obtained for 25 cents from the American Standards Association, 29 West 39th St., New York 18, N. Y.



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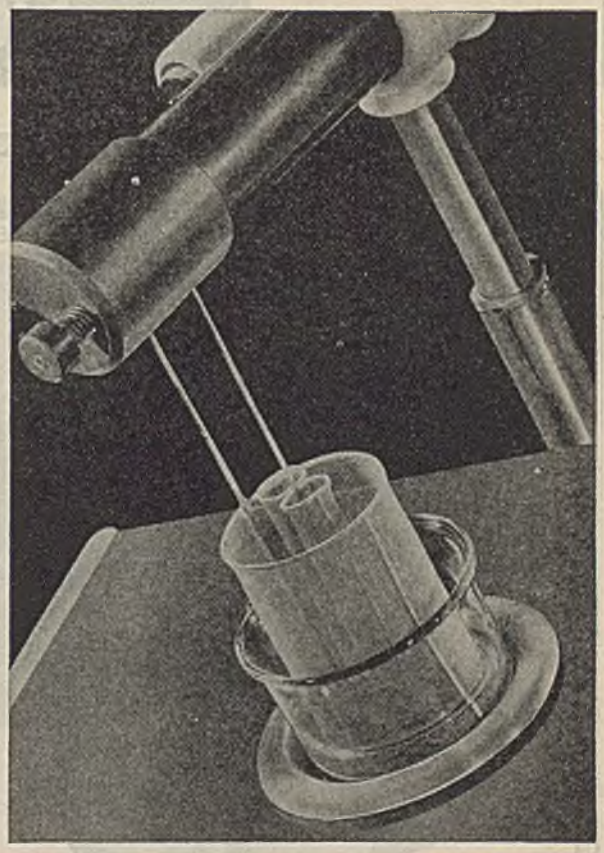

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