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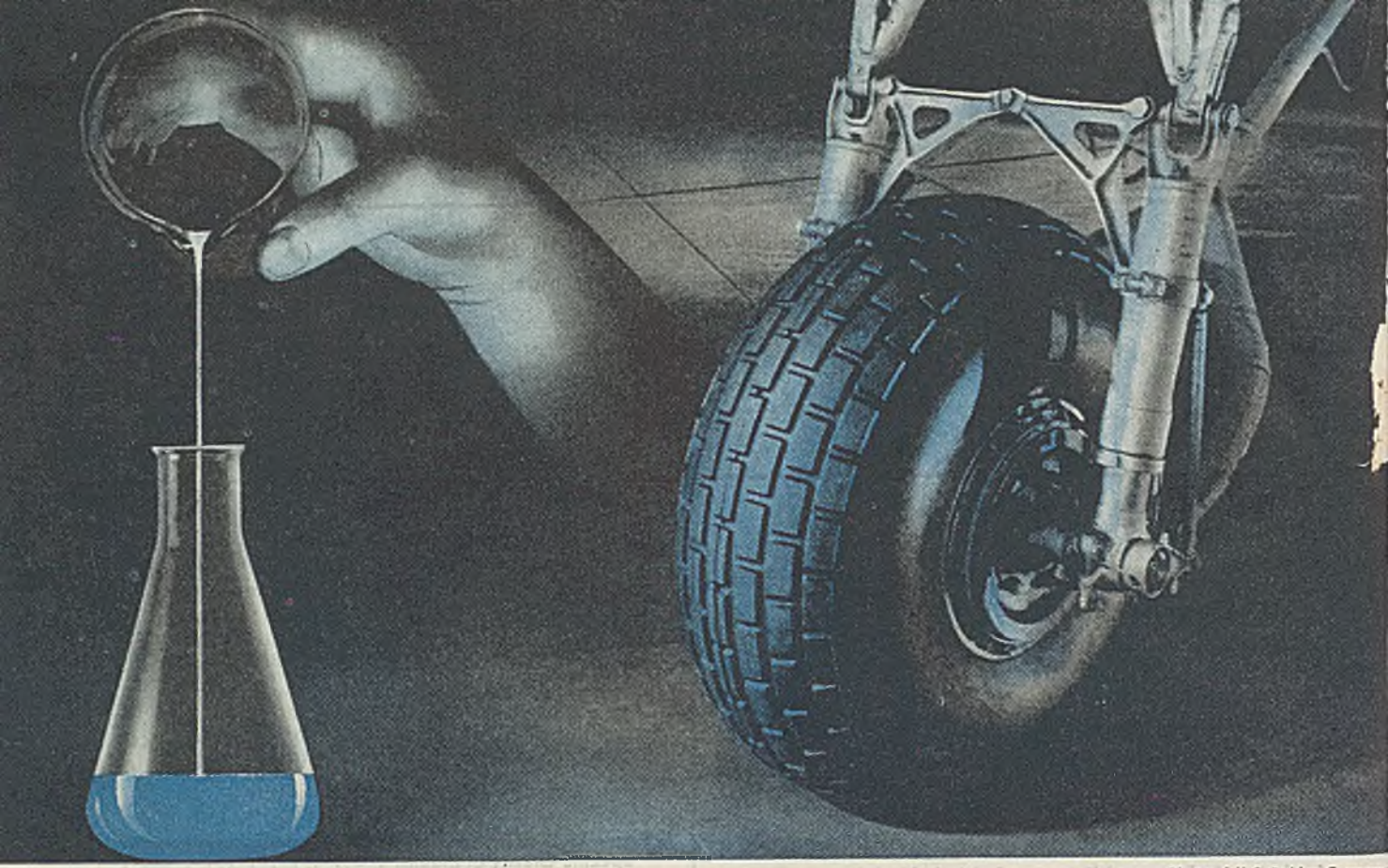

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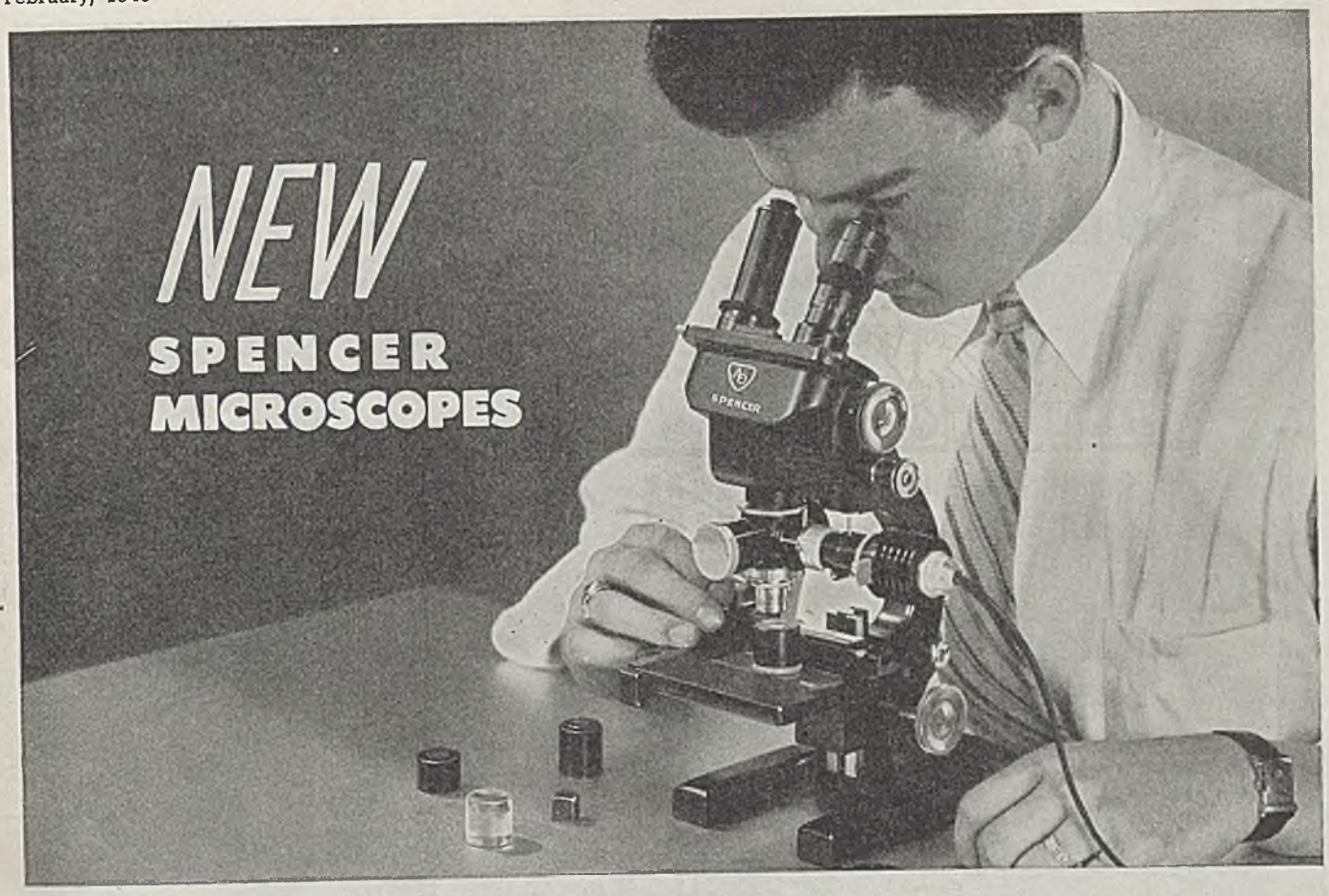

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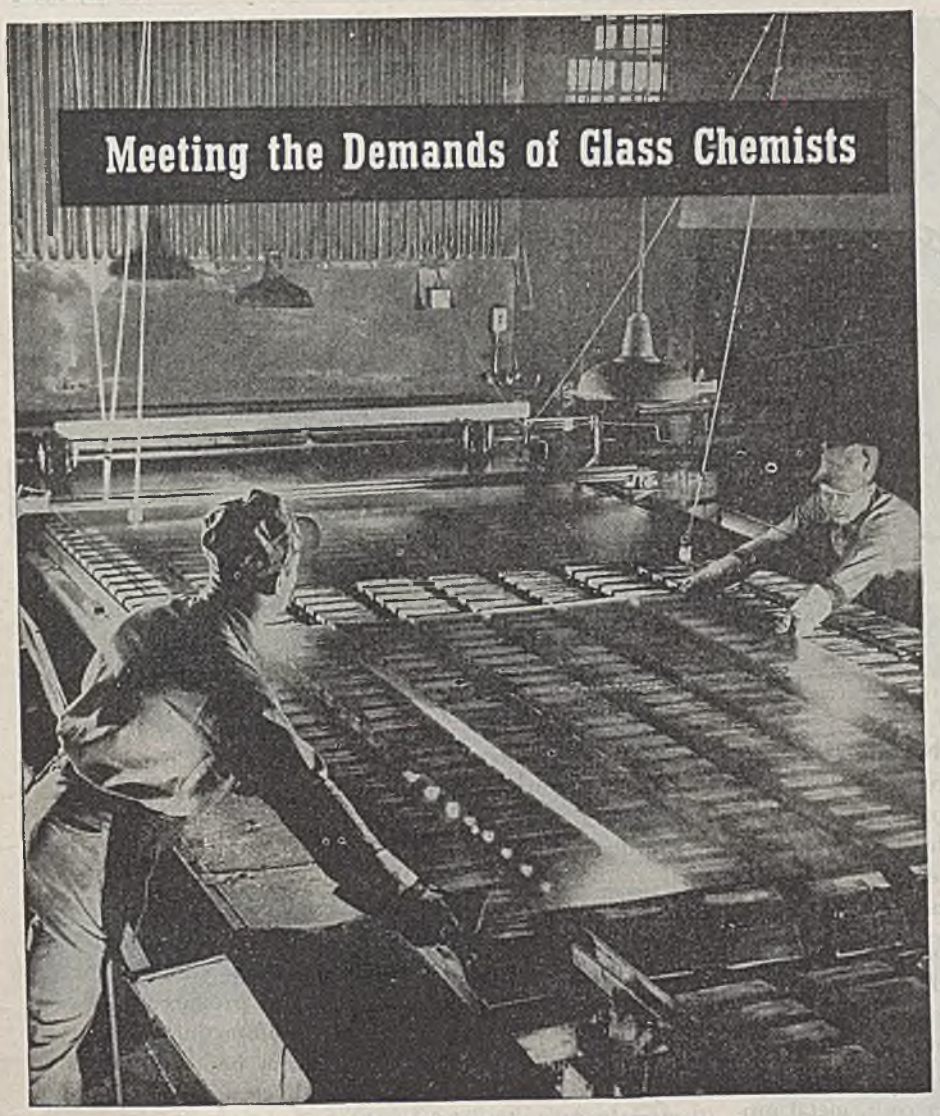

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Nitrogen compounds (as N)	0.001 %
Phosphate (PO_4)	0.002 %
Sulfur compounds (as SO_4)	0.004 %
NH_4OH precipitate and Silica	0.01 %
Silica (SiO_2)	0.005 %
Arsenic (As)	0.0000%
Calcium & Magnesium precip.	0.01 %
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Sulfate (SO_4)	0.005 %
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Non-volatile	0.005 %
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Fluorine (F)	0.0001%
Nitrogen compounds (as N)	0.003 %
Sulfate (SO_4)	0.005 %
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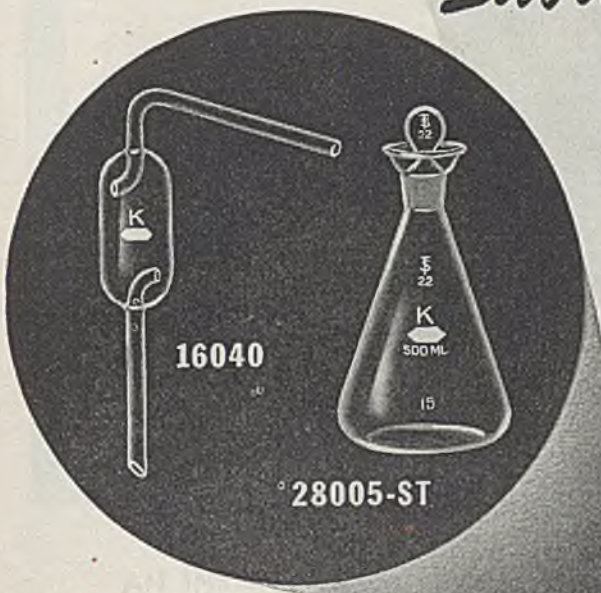

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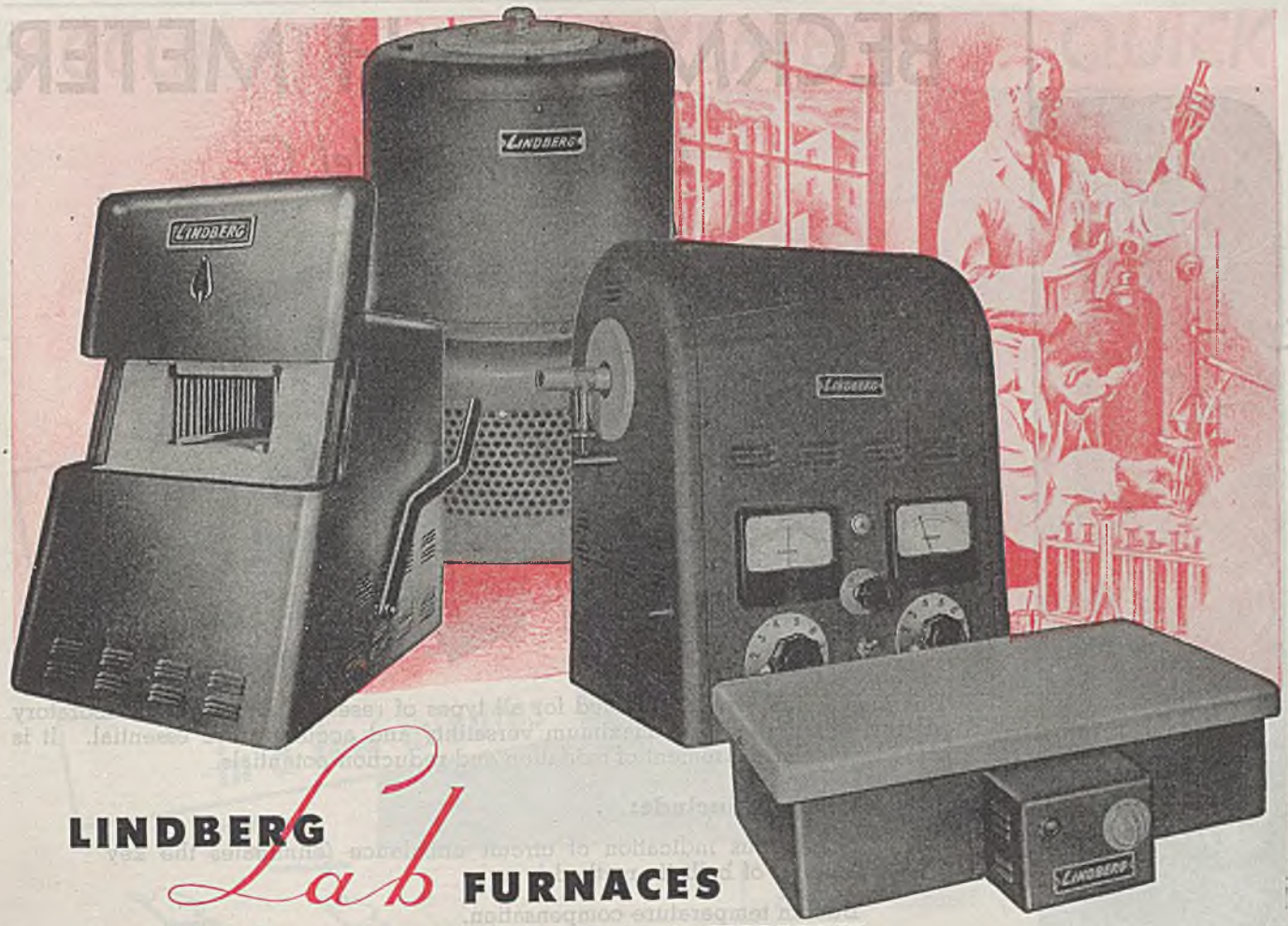

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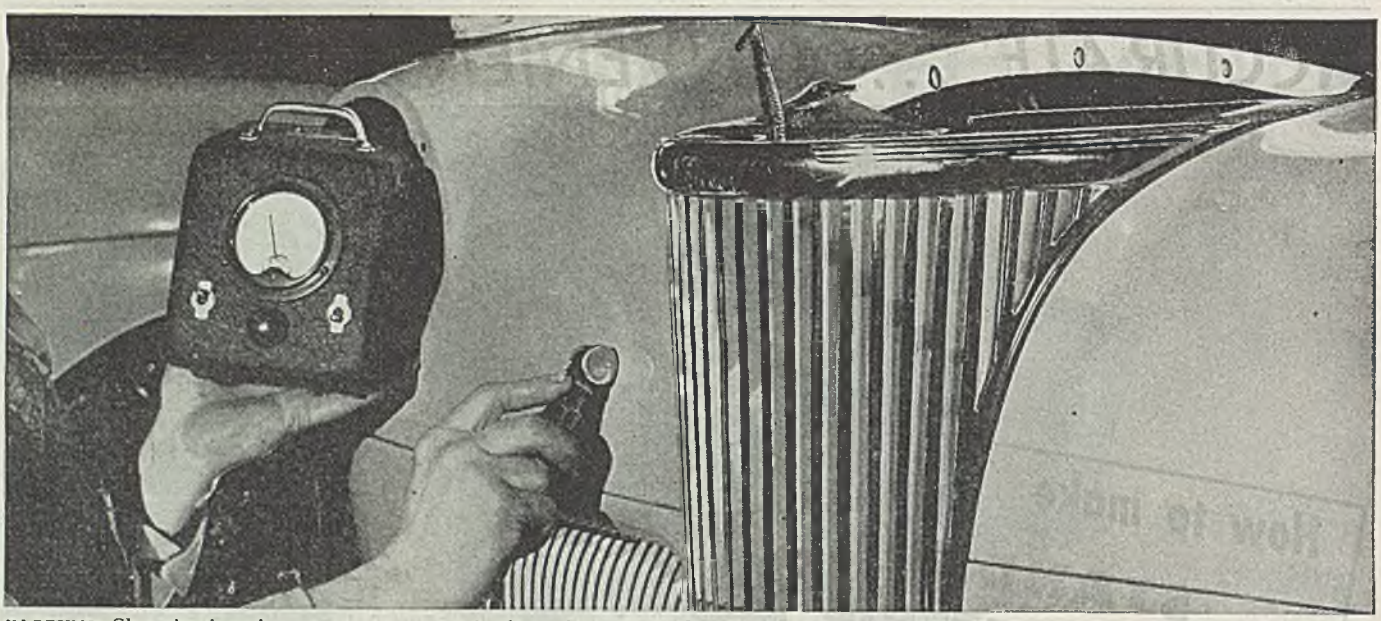

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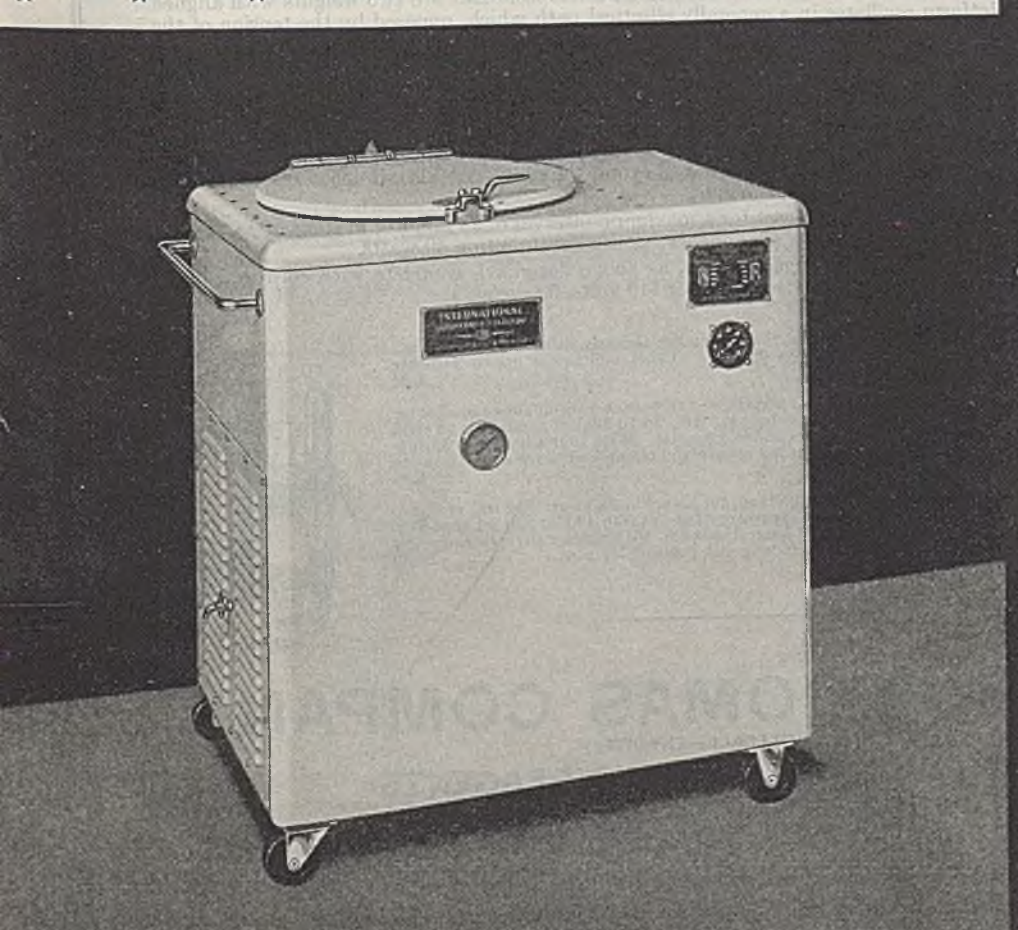

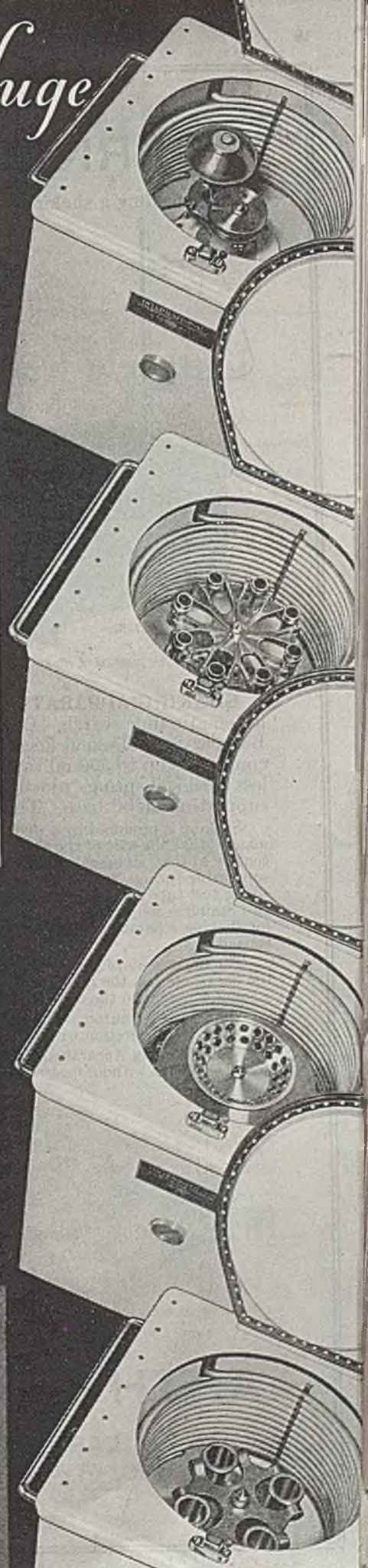

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Tabulated Diffraction Data for Tetragonal Isomorphs

L. K. FREVEL, H. W. RINN, AND H. C. ANDERSON, The Dow Chemical Company, Midland, Mich.

COMPOUND analysis of crystalline solids by isomorphism depends for its utility on the availability of systematically arranged representative diffraction patterns of the various known crystal structures. The tabulation of the cubic structures (*3*) has been found useful and the effectiveness of the method has prompted the compilation of the tetragonal structures. The procedure for comparing diffraction patterns of isomorphous substances has been described adequately (*4*), hence only the tabulated diffraction data for tetragonal isomorphs are presented in this paper.

Figures 1, 2, 3, and 4 depict representative diffraction patterns of 40 tetragonal structures designated as in the "Strukturbericht" (*2*, *5-9*). The patterns are arranged in sets and within each set the simplest structure with the highest symmetry (*11*) is listed first. The averaged relative intensities, based largely on the Dow file of standards, refer to Debye-Scherrer-Hull patterns taken with MoKα radiation. For each structure only reflections compatible with the respective space group are shown. The intensities of superposed lines were resolved by calculating the appropriate structure factors. To round out the available powder data, some fifty substances were synthesized and their diffraction patterns carefully indexed.

GENERAL PROCEDURE FOR IDENTIFYING A NONCATALOGED PATTERN

(1) Plot the log d values and corresponding relative intensities of the unidentified pattern on a narrow strip of paper; (2) verify that the pattern is noncubic (*3*); (3) find an isomorphic prototype among the representative diffraction patterns for the anisotropic crystal structures; (4) compute the lattice constants and check the appropriate classification tables (for the tetragonal system check Tables III and IV); (5) confirm the identification of the unknown phase by a qualitative spectroscopic analysis or by spot tests.

The following example illustrates the procedure:

Table I. X-Ray Powder Diffraction Data

d, kX	$\frac{I}{\bar{I}_1}$	$\{hkl\}$
7.25	0.06	001
3.75	1.00 (100)	101
3.60	0.15	002
3.10	1.00 (100)	110
(2.98)	(0.01)	
2.78	0.63	102
2.35	0.75 (75)	112
2.19	0.63	200
2.11	0.25	201, 103
1.90	0.40	211, 113
1.72	0.25	212
1.68	0.20	104
1.62	0.02	203
(1.59)	(0.01)	
1.55	0.15	220, 114
1.52	0.15	221, 213
1.43	0.08	222, 301
1.39	0.10	204, 310
1.355	0.02	311, 302

Filtered MoKα was used to obtain the powder diffraction data. d = nterplanar spacing. $\frac{I}{\bar{I}_1}$ = relative intensity. The lattice constants for the unknown phase are $a = 4.38\ kX$, $c = 7.23\ kX$; $\frac{c}{a} = 1.65$.

Table II. Statistical Data on Tabulated Tetragonal Substances

Dominant structures	HO_4, C4, C11, OB20, ...
N_r = number of examples	36, 33, 18, 17, ...
$\frac{N_r}{\Sigma_r N_r}$	0.11, 0.10, 0.06, 0.05, ...
Configurations favoring tetragonal symmetry	Tetrahedral, octahedral, square; linear; $4n$-cyclic
Prevalence of primitive lattices	53%
Prevalence of body-centered lattices	47%
n_{hk0} = average number of observed prism reflections per powder pattern	4.4; $1 \leq n_{hk0} \leq 9$
$\bar{\nu}_{hk0}$ = probability of observing $\{hk0\}$	$(\bar{\nu}_{110}, \bar{\nu}_{200}, \bar{\nu}_{220})$ = (0.65, 0.93, 0.90)
$\frac{\bar{I}_{hk0}}{\bar{I}_1}$ = average relative intensity of $\{hk0\}$	$\left(\frac{\bar{I}_{110}}{\bar{I}_1}, \frac{\bar{I}_{200}}{\bar{I}_1}, \frac{\bar{I}_{220}}{\bar{I}_1}\right)$ = (0.38, 0.51, 0.17)
$_n\{hkl\}$ = probability that $\{hkl\}$ is the n^{th} strongest powder reflection of a tetragonal structure	$\bar{\nu}_1\{101, 112, 110, 211, 200\}$ = (0.30, 0.22, 0.13, 0.13, 0.08) $\bar{\nu}_2\{101, 200, 211, 110, 112\}$ = (0.15, 0.13, 0.10, 0.08, 0.08) $\bar{\nu}_3\{110, 211, 101, 200, 112\}$ = (0.10, 0.10, 0.08, 0.08, 0.05)
$\frac{\bar{c}}{\bar{a}}$ = average axial ratio	1.51; $0.31 \leq \frac{c}{a} \leq 6.7$

Columns 1 and 2 of Table I give the powder diffraction data of a phase encountered in a magnesium flux sample. After plotting log d and the corresponding relative intensities on a strip of paper, one checks first the index scale for the cubic system (*3*) and finds that the substance is noncubic. Proceeding to the tetragonal system and comparing systematically the unknown pattern with those of Figures 1, 2, 3, and 4, one makes the following observations: The first indication of a fit with the data is noted for C11 with $\frac{c}{a} = 1.64$ ($a \approx 4.4\ kX$, $c \approx 7.2\ kX$). However, the lines 7.25, 2.78, 1.72, 1.68, 1.62 kX are not accounted for by this structure and the intensity agreement of the indexed lines is not satisfactory. Structure C38 permits indexing all the lines for $\frac{c}{a} = 1.65$ ($a = 4.38\ kX$, $c = 7.23\ kX$) but gives poor agreement with the relative intensities. Checking Table III under C38, one fails to find a substance agreeing with the computed lattice constants. A similar situation is encountered for structure $D3_1$ with $\frac{c}{a} = 2.32$ ($a = 6.20\ kX$, $c = 14.5\ kX$) and for structure DO_{22} with $\frac{c}{a} = 1.65$ ($a = 8.75\ kX$, $c = 14.5\ kX$). Structure EO_1, however, accounts for all the lines and matches the relative intensities well. Looking under EO_1 for $\frac{c}{a} = 1.65$ ($a = 4.38\ kX$, $c = 7.23\ kX$), one identifies the unknown as BaFCl. Spectroscopic analysis confirms Ba as a major constituent. The faint lines 2.98 and 1.59 kX belong to an unidentified material present in low concentration. (In completing the comparison of the identified pattern with the remaining tetragonal structures, one finds only partial matching with structures HO_4, HO_7, and HO_8.)

An alternative method of identifying the unknown phase is based on the general tabulation of tetragonal substances in Table IV. By matching the unknown pattern against the standard structures it is noted that the pattern can be indexed tetragonal with $\frac{c}{a} = 1.65$ ($a = 4.38$ kX, $c = 7.23$ kX). Looking in Table IV for these lattice constants one finds BaFCl listed. As in the first method a qualitative spectroscopic analysis is required to confirm the phase identification. In using Table IV it is advisable to look not only under $\frac{c}{a}$ but also under $\left(\frac{2^r p}{q}\right)\frac{c}{a}$ where $p, q = 1,2,3,\ldots,n$ and $r = 0, \pm\frac{1}{2}$. In practice one usually considers only the factors $2, \sqrt{2}, \frac{1}{\sqrt{2}}, \frac{1}{2}$.

The ease with which a tetragonal pattern can be recognized is a determining factor in the speed of the above methods. Reference to Table II suggests how one may expedite the indexing of tetragonal powder patterns. For approximately 85% of the tetragonal substances it is possible to pick out the {200} and {220} reflections by translating the log d strip of the unknown pattern along the {hko} scale at the top of Figure 1. The data of Table I can be used to illustrate the procedure. After plotting log d one fixes the first line, $d_1 = 7.25$ kX, on {200} of the {hko} scale and notes if any of the remaining d's match {220}. As no match is found one proceeds systematically to the succeeding lines and observes that $d_4 = 3.10$ kX and $d_8 = 2.19$ kX match—i.e., $d_4:d_8 = 1.415 \approx \sqrt{2} = d_{\{200\}}:d_{\{220\}} = d_{\{110\}}:d_{\{200\}}$. Checking the possibility that $d_4:d_8 = d_{\{110\}}:d_{\{200\}}$, one sees immediately that $d_4:d_8:d_{15} = 3.10:2.19:1.55 = d_{\{110\}}:d_{\{200\}}:d_{\{220\}} = 2:\sqrt{2}:1$. Three prism reflections are thus identified and the unknown pattern is readily indexed by following the {110} lines down Figure 1 until a match is found for $\frac{c}{a} = 1.65$. The phase identification is then carried out in the manner already discussed.

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Table III. Tetragonal Substances Tabulated by Types

Table III lists 329 tetragonal substances. For each isomorphous type the members are arranged in the ascending order of their axial ratios. If two members have the same value for c/a the one with the smaller lattice constants is listed first. (To avoid repetition, the various literature values have been averaged.) For specific references prior to 1939 see "Strukturbericht", Vols. I to VII; for later references see *Chem. Abst.*, 33 to 39 (1939–1945).

$\frac{c}{a}$	a, kX	c, kX	Substance
		A5	
0.5456	5.819	3.175	β-Sn
		A6	
0.936	3.774	3.533	γ-Mn
0.952	3.76	3.58	95Mn.5Cu
0.962	3.767	3.624	89Mn.11Cu
0.981	3.764	3.693	79Mn.21Cu
0.998	3.752	3.744	66Mn.34Cu
1.077	4.585	4.937	In
		B10	
1.22	3.55	4.33	LiOH
1.26	3.98	5.01	PbO (red)
1.27	3.80	4.81	SnO
		B17	
1.74	3.03	5.26	PdO
1.76	3.03	5.32	PtO
1.76	3.47	6.10	PtS
		B25 and OB25	
0.667	6.011	4.009	NH_4SH
0.707	6.18	4.37	γ-NH_4I
0.709	5.70	4.04	γ-NH_4Br($\sim$173° K.)
0.711	7.78	5.53	$N(CH_3)_4Cl$
0.712	8.44	6.01	$N(CH_3)_4MnO_4$
0.713	7.76	5.53	$N(CH_3)_4Br$
0.722	8.28	5.98	$N(CH_3)_4ClO_4$
0.724	7.94	5.75	$N(CH_3)_4I$
0.729	6.34	4.62	PH_4I
		B34	
1.03	6.37	6.58	(Pd, Pt, Ni)S
1.04	6.35	6.60	PdS
		B37	
0.873	8.02	7.00	TlSe
		NaBi	
1.35	3.24	4.38	MgIn
1.39	3.46	4.80	NaBi
		C4	
0.570	(4.86)	(2.77)	WO_2
0.574	(4.86)	(2.79)	MoO_2
0.621	4.77	2.96	CbO_2
0.633	4.61	2.92	$RhVO_4$
0.634	4.54	2.88	VO_2
0.642	4.69	3.01	$RhCbO_4$
0.644	4.58	2.95	TiO_2
0.645	4.68	3.02	$RhTaO_4$
0.649	4.41	2.86	CrO_2
0.649	4.64	3.01	$CrCbO_4$
0.650	4.63	3.01	$CrTaO_4$
0.651	4.39	2.86	GeO_2
0.652	4.40	2.87	MnO_2
0.652	4.62	3.01	$FeSbO_4$
0.652	4.67	3.04	$FeTaO_4$
0.652	4.68	3.05	$FeCbO_4$
0.656	4.51	2.96	$AlSbO_4$
0.659	4.64	3.06	MgF_2
0.660	4.59	3.03	$GaSbO_4$
0.660	4.71	3.11	NiF_2
0.664	4.58	3.04	$CrSbO_4$
0.665	4.72	3.14	ZnF_2
0.672	4.72	3.17	SnO_2
0.674	4.60	3.10	$RhSbO_4$
0.678	4.87	3.30	MnF_2
0.679	4.70	3.19	CoF_2
0.683	4.95	3.38	PbO_2
0.686	4.93	3.38	PdF_2
0.690	4.51	3.11	RuO_2
0.696	4.83	3.36	FeF_2
0.699	4.49	3.14	IrO_2
0.707	4.51	3.19	OsO_2
0.787	(4.79)	(3.77)	TeO_2
		C5	
2.51	3.75	9.43	TiO_2
		C11	
1.15	6.27	7.22	CsO_2
1.17	5.99	7.02	RbO_2
1.18	5.70	6.73	KO_2
1.20	...	...	UC_2
1.28	(4.14)	(5.28)	ThC_2
1.61	4.39	7.05	BaC_2
1.63	4.11	6.68	SrC_2
1.65	3.82	6.30	NdC_2
1.65	3.87	6.37	CaC_2
1.66	3.85	6.38	PrC_2
1.67	3.54	5.91	CaO_2
1.67	3.75	6.28	SmC_2
1.67	3.87	6.48	CeC_2
1.67	3.92	6.55	LaC_2

(*Continued on next page*)

Table III (*Continued*)

$\frac{c}{a}$	a, kX	c, kX	Substance
1.79	3.78	6.77	BaO_2
1.85	3.55	6.55	SrO_2
1.97	(4.28)	(8.42)	KHC_2
2.10	(3.89)	(8.17)	$NaHC_2$
		C13	
2.83	4.36	12.36	HgI_2
		C16	
0.806	6.052	4.878	Al_2Cu
0.814	6.52	5.31	Sn_2Fe
0.818	6.647	5.434	Sn_2Mn
0.832	5.099	4.240	Fe_2B
0.841	5.006	4.212	Co_2B
0.846	5.899	4.991	Ge_2Fe
0.851	4.980	4.236	Ni_2B
0.852	6.835	5.821	Pb_2Pd
0.857	6.348	5.441	Sn_2Co
0.880	6.651	5.853	Pb_2Rh
		C20	
2.45	3.21	7.88	WSi_2
2.46	3.20	7.86	$MoSi_2$
		C30	
1.40	4.96	6.92	SiO_2
1.41	5.00	7.06	$AlPO_4$
		C38	
1.53	3.992	6.091	Cu_2Sb
1.61	4.08	6.56	Mn_2Sb
1.65	3.627	5.973	Fe_2As
1.67	3.76	6.27	Mn_2As
1.75	3.613	6.333	Cr_2As
		C47	
0.605	8.35	5.05	SeO_2
		C48	
2.88	2.998	8.630	Cr_2Al
		ZnP_2	
3.68	5.07	18.65	ZnP_2
3.73	5.28	19.70	CdP_2
		DO_{22}	
1.46	5.548	8.093	$TiGa_2$
1.55	5.605	8.712	$ZrGa_2$
1.56	5.334	8.305	VAl_2
1.57	5.422	8.536	$TaAl_2$
1.58	5.425	8.579	$TiAl_2$
1.58	5.427	8.584	$CbAl_2$
		DO_{23}	
4.32	4.003	17.29	$ZrAl_2$
		$D1_1$	
2.46	4.53	11.14	Al_4Ba
2.48	4.45	11.04	Al_4Sr
2.54	4.35	11.07	Al_4Ca
		$D3_1$	
2.36	4.92	11.62	Hg_2I_2
2.39	4.65	11.10	Hg_2Br_2
2.44	4.46	10.89	Hg_2Cl_2
2.98	3.66	10.9	Hg_2F_2
		$D5_3$	
1.40	8.75	12.28	Cd_3P_2
1.41	8.10	11.45	Zn_3P_2
1.41	8.32	11.76	Zn_3As_2
1.41	8.95	12.65	Cd_3As_2
		Fe_2P	
0.490	9.09	4.45	Fe_2P
0.491	9.01	4.42	$(Fe, Ni, Go)_2P$
0.492	8.92	4.39	Ni_2P
0.499	9.13	4.56	Cr_2P
0.502	9.16	4.60	Mn_2P
		EO_1	
1.65	4.38	7.22	BaFCl
1.68	4.10	6.88	SrFCl
1.71	4.65	7.93	BaFI
1.76	3.89	6.83	CaFCl
1.76	4.09	7.21	PbFCl
1.82	4.18	7.59	PbFBr
1.89	3.89	7.37	BiOCl
2.07	3.92	8.11	BiOBr
2.28	4.01	9.14	BiOI
		$E1_1$	
1.82	5.66	10.30	$AgFeS_2$
1.97	5.26	10.37	$CuFeS_2$

$\frac{c}{a}$	a, kX	c, kX	Substance
		$E1_4$	
0.550	10.81	5.94	$(PnCl_2)_4$
		$E2_2$	
1.89	4.19	7.94	NH_4HgCl_3
		$E2_6$	
0.502	13.30–13.52	6.69–6.78	$KMg(H_2O)_6(Cl, Br)_3$
		($E3_1$)	
1.00	6.34	6.34	Ag_2HgI_4
1.01	6.08	6.14	Cu_2HgI_4
		($E6_1$)	
0.906	(6.41)	(5.81)	$Sr(OH)_2.8H_2O$
		($E6_2$)	
0.880	(6.32)	(5.56)	$SrO_2.8H_2O$
		$FeTa_2O_6$	
1.94	4.70	9.10	$NiTa_2O_6$
1.94	4.71	9.12	$Fe(Cb, Ta)_2O_6$
1.94	4.73	9.16	$CoTa_2O_6$
1.95	4.70	9.18	$MgTa_2O_6$
1.95	4.71	9.18	$FeTa_2O_6$
		$F1_1$	
0.921	9.69	8.92	$Hg(CN)_2$
		$F5_3$	
1.16	6.07	7.03	KNCO
1.16	6.09	7.06	KN_3
1.17	6.36	7.41	RbN_3
1.20	5.67	6.81	KFHF
		$F5_4$	
0.593	6.31	3.74	NH_4ClO_3
		GO_1	
0.871	5.74	5.00	NH_4NO_3-II (357–398° K.)
		Phosgenite	
1.086	8.13	8.83	$Pb_2Cl_2CO_3$
1.086	8.34	9.06	$Pb_2Br_2CO_3$
		HO_1	
0.867	7.13	6.18	YVO_4
0.874	7.25	6.34	$CaCrO_4$
0.888	6.87	6.10	YPO_4
0.901	6.58	5.93	$ZrSiO_4$
0.910	6.89	6.27	$YAsO_4$
1.46	(7.74)	(11.31)	$Y(Cb, Ta)O_4$
1.46	(7.76)	(11.32)	$YCbO_4$
1.47	(7.75)	(11.41)	$YTaO_4$
		HO_4	
2.15	5.94	12.80	NH_4IO_4
2.17	5.15	11.17	$CdMoO_4$
2.17	5.24	11.38	$CaWO_4$
2.17	5.35	11.63	$NaLa(WO_4)_2$
2.18	5.32	11.59	$NaCe(WO_4)_2$
2.18	5.34	11.63	$LiLa(WO_4)_2$
2.19	5.23	11.44	$CaMoO_4$
2.19	5.27	11.55	$NaBi(MoO_4)_2$
2.19	5.36	11.72	$NaReO_4$
2.20	5.23	11.50	$LiBi(MoO_4)_2$
2.20	5.31	11.67	$LiLa(MoO_4)_2$
2.20	5.33	11.70	$NaLa(MoO_4)_2$
2.20	5.40	11.90	$SrWO_4$
2.20	5.75	12.63	KIO_4
2.20	5.87	12.94	$RbIO_4$
2.20	5.87	12.94	NH_4ReO_4
2.21	5.44	12.01	$PbWO_4$
2.21	5.44	12.03	$KLa(WO_4)_2$
2.22	5.38	11.92	$KBi(MoO_4)_2$
2.22	5.39	11.94	$KCe(WO_4)_2$
2.22	5.62	12.50	$KReO_4$
2.23	5.35	11.92	$AgReO_4$
2.23	5.37	11.96	$SrMoO_4$
2.23	5.41	12.08	$PbMoO_4$
2.23	5.42	12.11	$KLa(MoO_4)_2$
2.24	5.32	11.93	$NaIO_4$
2.24	5.37	12.01	$AgIO_4$
2.26	5.62	12.70	$BaWO_4$
2.27	5.80	13.17	$RbReO_4$
2.29	5.56	12.76	$BaMoO_4$
2.30	5.08	11.69	$BiAsO_4$
2.31	5.76	13.33	β-$TlReO_4$ (400° K.)
2.32	5.65	13.08	$KOsO_3N$
2.36	5.46	12.89	$KCrO_3F$
2.52	5.61	14.13	$CsSO_3F$
2.53	5.72	14.50	$CsCrO_3F$

(*Continued on page 87*)

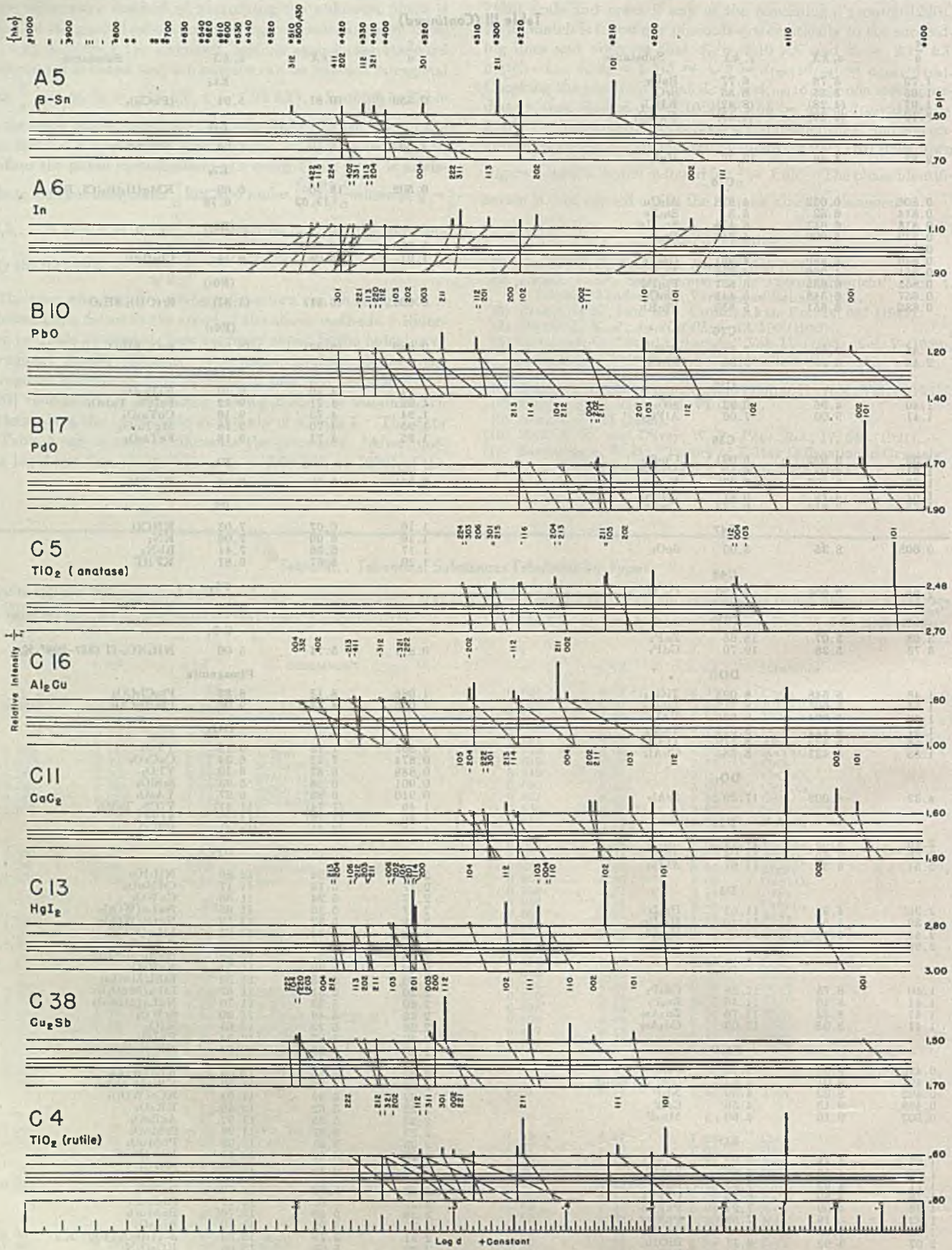

Figure 1. Representative Diffraction Patterns of Tetragonal Structures

The log d_{hko} values of the various structures (Figures 1, 2, 3, and 4) are matched according to the $\{hko\}$ reflections. (To conserve printing space some of the structures had to be translated to the left—e.g., *B10, C13, C38.*) The relative intensities of the powder pattern pertaining to a particular structure represent the arithmetically averaged relative intensities (for MoKα radiation) of representative members of the isomorphous group. The change of d_{AH} with c/a is expressed graphically (*1, 10*) and covers the c/a spread encountered within the particular isomorphous group

Table III (*Continued*)

$\frac{c}{a}$	a, kX	c, kX	Substance
		HO_7	
1.524	4.459	6.796	$BAsO_4$
1.533	4.332	6.640	BPO_4
		HO_8	
1.73	3.55	6.14	$KAlF_4$
1.73	3.62	6.26	$RbAlF_4$
1.76	3.61	6.37	$TlAlF_4$
1.77	3.59	6.35	NH_4AlF_4
		$(H1_1)$	
1.48	5.85	8.68	$CuFe_2O_4$
1.58	6.20	9.82	$CaIn_2O_4$
1.59	5.74	9.15	$ZnMn_2O_4$
1.61	6.12	9.87	$CdIn_2O_4$
1.64	5.75	9.42	$MnMn_2O_4$
		$PbPb_2O_4$	
0.684	8.22	5.62	$NiAs_2O_4$
0.687	8.592	5.905	$FeSb_2O_4$
0.689	8.685	5.980	$MnSb_2O_4$
0.696	8.49	5.91	$CoSb_2O_4$
0.697	8.491	5.920	$ZnSb_2O_4$
0.699	8.445	5.907	$MgSb_2O_4$
0.708	8.35	5.91	$NiSb_2O_4$
0.722	8.72	6.30	$SnPb_2O_4$
0.742	8.85	6.57	$PbPb_2O_4$
		$H1_6$	
0.582	7.04	4.10	K_2PdCl_4
0.591	6.99	4.13	K_2PtCl_4
0.591	7.21	4.26	$(NH_4)_2PdCl_4$
		$H2_2$	
0.936	7.61	7.12	KH_2AsO_4
0.938	7.43	6.97	KH_2PO_4
1.003	7.52	7.54	$NH_4H_2PO_4$
1.005	7.70	7.74	$NH_4H_2AsO_4$
		$H2_6$	
1.97	5.46	10.73	Cu_2FeSnS_4
		$H4_1$	
1.024	7.81	8.00	$Rb_2CuCl_4.2H_2O$
1.05	7.58	7.96	$(NH_4)_2CuCl_4.2H_2O$
1.05	7.9	8.3	$(NH_4)_2CuBr_4.2H_2O$
1.06	7.45	7.88	$K_2CuCl_4.2H_2O$
1.09	7.50	8.16	$(NH_4)_2FeCl_4.2H_2O$
		$H4_3$	
0.403	10.40	4.19	$Pt(NH_3)_4Cl_2.H_2O$
0.423	10.21	4.31	$Pd(NH_3)_4Cl_2.H_2O$
		$H4_{17}$	
0.753	8.43	6.35	$Ag_2SO_4.4NH_3$
		$H5_3$	
2.95	6.99	20.63	$Ca(UO_2)_2(PO_4)_2.10^1/_2H_2O$
		$H5_{16}$	
1.21	6.98	8.42	$Ca(UO_2)_2(PO_4)_2.6^1/_2H_2O$
		$La_2(MoO_4)_3$	
2.18	5.32	11.60	$Pr_2(MoO_4)_3$
2.19	5.29	11.58	$Nd_2(MoO_4)_3$
2.21	5.33	11.78	$Ce_2(MoO_4)_3$
2.21	5.35	11.84	$La_2(MoO_4)_3$
2.23	5.22	11.62	$Sm_2(MoO_4)_3$
		$NaBaPO_4$	
0.847	9.76	8.27	$NaBaPO_4$
0.848	9.84	8.34	$KBaPO_4$
0.857	9.25	7.93	$NaSrPO_4$
0.859	9.50	8.16	$KSrPO_4$
		$J1_4$	
1.25	6.99	8.75	$K_2O_3O_2Cl_4$
		$J1_9$	
1.50	6.97	10.43	$AgCo(NH_3)_2(NO_2)_4$
		$J1_{11}$	
0.974	8.12	7.91	$AgSb(OH)_6$
0.984	8.01	7.88	$NaSb(OH)_6$
		$J3_1$	
1.14	15.84	18.01	$K_2TlCl_6.2H_2O$
1.15	16.95	19.45	$Rb_2TlBr_6.8/7H_2O$
		$K3_1$	
1.58	9.18	14.47	Cs_2CoCl_5
1.61	8.7	14.0	Rb_2CoCl_5

$\frac{c}{a}$	a, kX	c, kX	Substance
		$K3_4$	
1.71	8.39	14.34	$NH_4Pb_2Br_5$
1.72	8.41	14.5	$RbPb_2Br_5$
1.73	8.14	14.1	KPb_2Br_5
		$K7_8$	
1.48	7.01	10.36	$Na_3Al_2F_{14}$
		$K7_8$	
1.45	7.49	10.87	$Cs_2AuAuCl_8$
1.49	7.38	11.01	$Cs_2AgAuCl_6$
		K_2CrO_3	
1.13	6.70	7.60	K_2CrO_3
1.13	7.37	8.34	Cs_2TaO_3
1.14	7.05	8.05	Rb_2TaO_3
1.16	6.78	7.86	K_2CbO_3
1.16	6.78	7.88	K_2TaO_3
		$LiBi_2O_4Cl_2$	
3.13	3.840	12.03	$LiBi_2O_4Cl_2$
3.13	3.877	12.13	$NaBi_2O_4Cl_2$
3.20	3.925	12.55	$NaBi_2O_4Br_2$
3.20	3.943	12.62	$Cd_2Bi_2O_4Br_2$
3.22	3.876	12.47	$LiBi_2O_4Br_2$
3.34	3.970	13.24	$Cd_2Bi_2O_4I_2$
3.34	3.990	13.31	$NaBi_2O_4I_2$
3.35	3.941	13.19	$LiBi_2O_4I_2$
		L10	
0.825	3.89	3.21	NiZn
0.935	3.98	3.72	AuCu
0.966	3.85	3.72	FePd
0.967	3.66	3.54	NiMn
		$S2_2$	
0.757	15.63	11.83	$Ca_{10}Mg_2Al_6Si_3O_{24}(OH)_4$
		$S5_2$	
1.76	9.00	15.84	$KCa_4Si_8O_{20}F.8H_2O$
		$S5_3$	
0.637	7.83	4.99	$Ca_2ZnSi_2O_7$
0.651	7.76	5.05	$(Ca, Na)_2(Mg, Al)(Al, Si)_2O_7$
0.655	7.75	5.08	$Ca_2Al_2SiO_7$
0.659	(7.47)	(4.92)	$(Ca, Na)_3Be(Al, Si)_3(O, F)_7$
0.675	(7.38)	(4.98)	$(Ca, Na)_3BeSi_3(O, OH, F)_7$
		$S6_4$	
0.624	12.27	7.66	$Ca_4Al_6Si_6O_{24}(SO_4, CO_3)$
0.627	12.09	7.58	$Na_4Al_3Si_3O_{12}Cl$
		OB11	
0.632	9.18	5.80	$N(CH_3)_4ICl_2$
		OB20	
1.72	5.09	8.76	CH_3NH_3Br
1.75	5.11	8.96	CH_3NH_3I
2.95	5.18	15.3	$C_4H_9NH_3I$
2.96	5.02	14.85	$C_4H_9NH_3Cl$
3.03	5.02	15.23	$C_4H_9NH_3Br$
3.33	5.01	16.7	$C_5H_{11}NH_3Cl$
3.35	5.16	17.3	$C_5H_{11}NH_3I$
3.40	5.00	17.0	$C_5H_{11}NH_3Br$
3.78	5.16	19.50	$C_6H_{13}NH_3I$
3.93	4.98	19.55	$C_6H_{13}NH_3Cl$
4.02	4.93	19.8	$C_6H_{13}NH_3Br$
4.15	5.18	21.5	$C_7H_{15}NH_3I$
4.25	4.96	21.1	$C_7H_{15}NH_3Cl$
4.58	5.18	23.7	$C_8H_{17}NH_3I$
5.42	5.18	28.1	$C_{10}H_{21}NH_3I$
5.88	5.18	30.46	$C_{11}H_{23}NH_3I$
6.03	5.18	31.24	$C_{12}H_{25}NH_3I$
		OB21	
1.20	4.28	5.13	CH_3NH_3Cl
1.51	4.85	7.33	$C_3H_7NH_3I$
1.58	4.48	7.10	$C_3H_7NH_3Cl$
1.61	4.57	7.36	$C_3H_7NH_3Br$
		OB25 and OHO_6	
0.711	7.78	5.53	$N(CH_3)_4Cl$
0.712	8.44	6.01	$N(CH_3)_4MnO_4$
0.713	7.76	5.53	$N(CH_3)_4Br$
0.722	8.28	5.98	$N(CH_3)_4ClO_4$
0.724	7.94	5.75	$N(CH_3)_4I$
		$Tl(CH_3)_2I$	
2.81	4.78	13.43	$Tl(CH_3)_2I$
3.08	4.47	13.78	$Tl(CH_3)_2Br$
3.27	4.29	14.02	$Tl(CH_3)_2Cl$

(*Continued on page 89*)

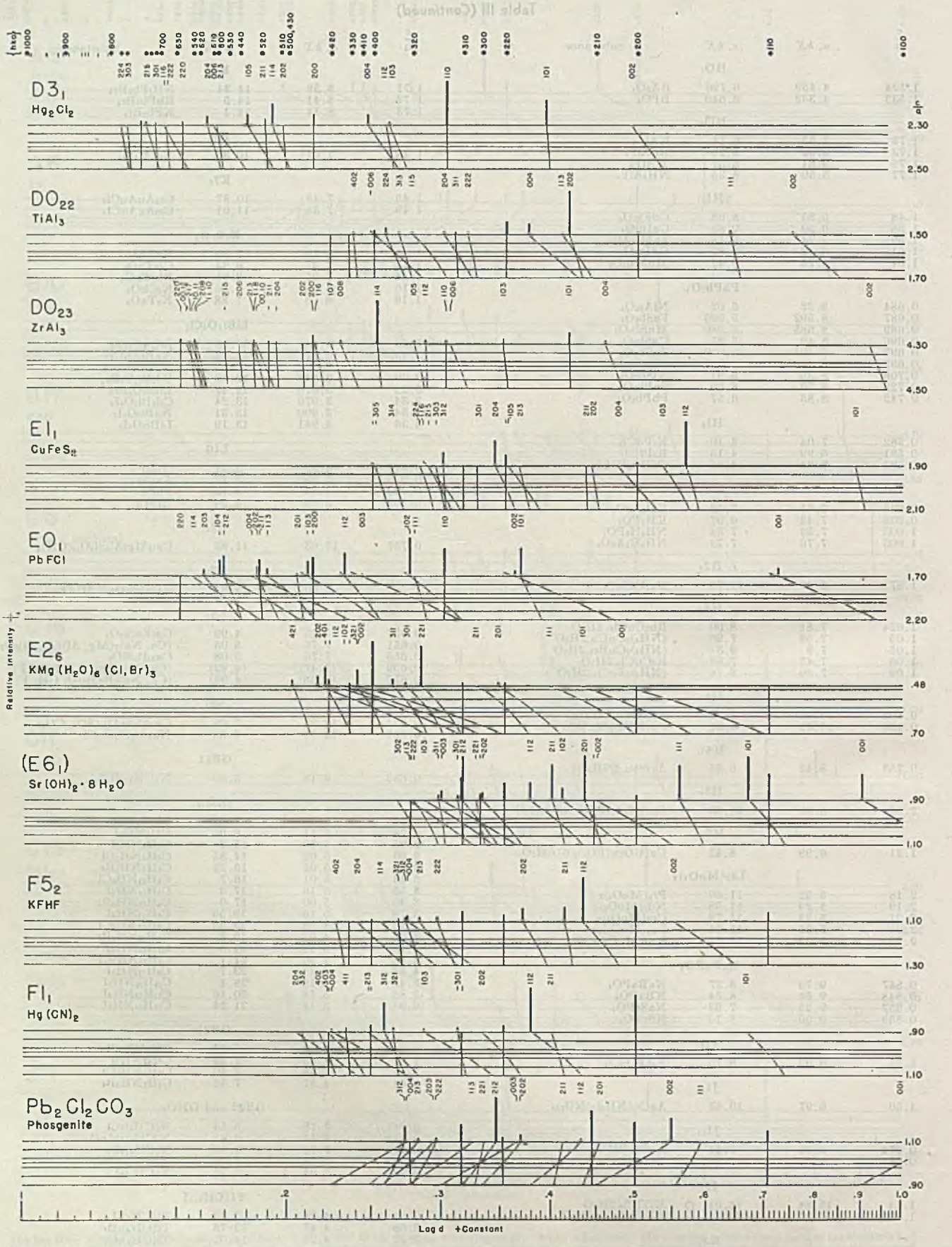

Figure 2. Representative Diffraction Patterns of Tetragonal Structures

Table III (*Continued*)

c/a	a, kX	c, kX	Substance
		OG1_2	
0.451	16.1	7.26	$[(CH_3)_3As, PdCl_2]_2$
0.451	16.6	7.48	$[(CH_3)_3As, PdBr_2]_2$
		OJ1_1	
1.42	7.88	11.19	$[N(CH_3)_4]_2SiF_6$
		$[(CH_3)_2SiO]_3$	
0.613	13.95	8.55	$[(CH_3)_2SiO]_3$
		O1_2	
0.396	10.37	4.11	$[CH_3CHO]_4$
		O2_4	
0.427	12.59	5.37	$Ag(CH_3.CS.NH_2)_4Cl$
0.444	12.43	5.52	$Cu(CH_3.CS.NH_2)_4Cl$
1.44	6.09	8.76	$C(CH_2OH)_4$
		O5	
0.457	12.1	5.53	$C(CH_2OCOCH_3)_4$
		O6	
0.533	12.15	6.48	$Pb(C_6H_5)_4$
0.544	11.90	6.47	$Sn(C_6H_5)_4$
0.591	11.60	6.85	$Ge(C_6H_5)_4$
0.612	11.44	7.00	$Si(C_6H_5)_4$
0.645	11.09	7.15	$C(C_6H_5)_4$
0.713	(9.38)	(6.69)	$C(CH_2ONO_2)_4$

Table IV. Tetragonal Substances Tabulated According to Axial Ratios

Table IV lists 447 tetragonal substances arranged in ascending order of their axial ratios. If two substances have the same value for c/a, the one with the smaller lattice constants is listed first. Column 4 also includes space group data where no definite structure has been established.

c/a	a, kX	c, kX	Type	Substance
0.311	12.2	3.79	...	$Na_{(0.2-0.4)}WO_3$
0.367	11.44	4.20	S_2^2-$I\bar{4}$	$Cd[Hg(CNS)_4]$
0.394	11.09	4.37	S_4^2-I4	$Co[Hg(CNS)_4]$
0.396	10.37	4.11	O1_2	$[CH_3CHO]_4$
0.401	11.06	4.43	S_4^2-I$\bar{4}$	$Zn[Hg(CNS)_4]$
0.403	10.40	4.19	$H4_8$	$Pt(NH_3)_4Cl_2.H_2O$
0.417	10.12	4.22	...	Be-(W,Mo)
0.422	10.21	4.31	$H4_8$	$Pd(NH_3)_4Cl_2.H_2O$
0.427	12.59	5.37	$O2_4$	$Ag(CH_3.CS.NH_2)_4Cl$
0.429	14.6	6.26	...	$MgPt(CN)_4.7H_2O$
0.444	12.43	5.52	$O2_4$	$Cu(CH_3.CS.NH_2)_4Cl$
0.451	16.1	7.26	OG1_2	$[(CH_3)_3As, PdCl_2]_2$
0.451	16.6	7.48	OG1_2	$[(CH_3)_3As, PdBr_2]_2$
0.457	12.1	5.53	O5	$C(CH_2OCOCH_3)_4$
0.464	8.12	3.77	...	CS_2(~100° K.)
0.487	18.8	9.15	C_{4h}^6-I$4_1/a$	$C_6H_4[1,2]CH_2.SO_2NH_3$
0.490	9.09	4.45	Fe_2P	Fe_2P
0.491	9.01	4.42	Fe_2P	$(Fe,Ni,Co)_2P$
0.492	8.92	4.39	Fe_2P	Ni_2P
0.495	7.56	3.74	...	W_4O_{11}
0.499	9.13	4.56	Fe_2P	Cr_2P
0.502	9.16	4.60	Fe_2P	Mn_2P
0.502	13.30–13.52	6.69–6.78	$E2_4$	$KMg(H_2O)_6(Cl,Br)_3$
0.514	34.04	17.49	D_{4h}^{14}-P4/*mnm*	NaK(Ca,Mg,Mn)-$Al_5Si_8O_{28}.8H_2O$, ashcroftine
0.518	5.56	2.88	...	CdHg
0.533	12.15	6.48	O6	$Pb(C_6H_5)_4$
0.536	12.78	6.85	C_{4h}^6-I$4_1/a$	$CH_2OH(CHOH)_2$-CH_2OH
0.541	26.60	14.40	...	$(C_5H_4[1,2]O.$-$CH{=}NOH)_2Pt$
0.544	11.90	6.47	O6	$Sn(C_6H_5)_4$
0.546	5.819	3.175	A5	β-Sn
0.550	10.81	5.94	$E1_4$	$[PNCl_2]_4$
0.550	12.17	6.69	...	$AgClO_3$
0.552	7.82	4.32	...	$ZnHg(CNS)_4$
0.570	(4.86)	(2.77)	C4	WO_2
0.574	(4.86)	(2.79)	C4	MoO_2
0.582	7.04	4.10	$H1_4$	K_2PdCl_4
0.582	12.19	7.09	S_4^2-I$\bar{4}$	$(C_6H_5)_4AsI$
0.591	6.99	4.13	$H1_6$	K_2PtCl_6
0.591	7.21	4.26	$H1_6$	$(NH_4)_2PdCl_6$
0.591	11.60	6.85	O6	$Ge(C_6H_5)_4$
0.593	6.31	3.74	F5_4	NH_4ClO_3
0.603	9.22	5.56	...	$Na_2Co(CNS)_4.8H_2O$, julienite
0.605	8.35	5.05	C47	SeO_2
0.612	11.44	7.00	O6	$Si(C_6H_5)_4$
0.613	13.95	8.55	$[(CH_3)_2SiO]_3$	$[(CH_3)_2SiO]_3$
0.617	4.81	2.97	C4	CbO_2
0.622	(5.72)	3.56	C_{4h}^5-I4/*m*	Ni_4Mo
0.624	12.27	7.66	S6$_4$	$Ca_4Al_6Si_6O_{24}(SO_4,CO_3)$, meionite
0.627	12.09	7.58	S6$_4$	$Na_4Al_3Si_3O_{12}Cl$, marialite
0.632	9.18	5.80	OB11	$N(CH_2)_4ICl_2$
0.633	4.61	2.92	C4	$RhVO_4$
0.634	4.54	2.88	C4	VO_2
0.637	7.83	4.99	S5$_2$	$Ca_2ZnSi_2O_7$, hardystonite
0.642	4.69	3.01	C4	$RhCbO_4$
0.644	4.58	2.95	C4	TiO_2
0.645	4.68	3.02	C4	$RhTaO_4$
0.645	11.09	7.15	O6	$C(C_6H_5)_4$
0.649	4.41	2.86	C4	CrO_2
0.649	4.64	3.01	C4	$CrCbO_4$
0.650	4.63	3.01	C4	$CrTaO_4$
0.651	4.39	2.86	C4	GeO_2
0.651	4.67	3.04	C4	$FeTaO_4$
0.651	7.76	5.05	S5$_2$	$(Ca,Na)_2(Mg,Al)$-$(Al_2Si)_2O_7$ melilite
0.652	4.40	2.87	C4	MnO_2
0.652	4.62	3.01	C4	$FeSbO_4$
0.652	4.68	3.05	C4	$FeCbO_4$
0.655	7.75	5.08	S5$_2$	$Ca_2Al_2SiO_7$, gehlenite
0.656	4.51	2.96	C4	$AlSbO_4$
0.659	4.64	3.06	C4	MgF_2
0.659	(7.47)	(4.92)	S5$_1$	$(Ca,Na)_2Be(Al,Si)_2$-$(O,F)_7$, meliphanite
0.660	4.59	3.03	C4	$GaSbO_4$
0.660	4.71	3.11	C4	NiF_2
0.664	4.58	3.04	C4	$CrSbO_4$
0.665	4.72	3.14	C4	ZnF_2
0.667	6.011	4.009	B25	NH_4SH
0.672	4.72	3.17	C4	SnO_2
0.674	4.60	3.10	C4	$RhSbO_4$
0.675	(7.38)	(4.98)	S5$_1$	$(Ca,Na)_2BeSi_2$-$(O,OH,F)_7$, leucophanite
0.678	4.87	3.30	C4	MnF_2
0.679	4.70	3.19	C4	CoF_2
0.683	4.95	3.38	C4	PbO_2
0.684	8.22	5.62	$PbPb_2O_4$	$NiAs_2O_4$
0.684	12.32	8.43	...	$C(CH_2OC_6H_5)_4$
0.686	4.93	3.38	C4	PdF_2
0.687	8.592	5.905	$PbPb_2O_4$	$FeSb_2O_4$
0.689	8.685	5.980	$PbPb_2O_4$	$MnSb_2O_4$
0.690	4.51	3.11	C4	RuO_2
0.696	4.83	3.36	C4	FeF_2
0.696	8.49	5.91	$PbPb_2O_4$	$CoSb_2O_4$
0.697	8.491	5.920	$PbPb_2O_4$	$ZnSb_2O_4$
0.699	4.49	3.14	C4	IrO_2
0.699	8.445	5.907	$PbPb_2O_4$	$MgSb_2O_4$
0.707	4.51	3.19	C4	OsO_2
0.707	6.18	4.37	B25	γ-NH_4I
0.708	8.35	5.91	$PbPb_2O_4$	$NiSb_2O_4$
0.709	5.70	4.04	B25	γ-NH_4Br (~173° K.)
0.711	7.78	5.53	OB25	$N(CH_3)_4Cl$
0.712	8.44	6.01	OB25	$N(CH_3)_4MnO_4$
0.713	7.76	5.53	OB25	$N(CH_3)_4Br$
0.713	(9.38)	(6.69)	O6	$C(CH_2ONO_2)_4$
0.715	8.56	6.12	A18	Cl_2 (88° K.)
0.718	10.15	7.29	D_4^6-P4_22_1	$Os_3C_4(CH_3)_3$
0.718	12.04	8.65	...	$Ca(OCl)_2.3H_2O$
0.722	8.28	5.98	OB25	$N(CH_3)_4ClO_4$
0.722	8.72	6.30	$PbPb_2O_4$	$SnPb_2O_4$
0.724	7.94	5.75	OB25	$N(CH_3)_4I$
0.729	6.34	4.62	B25	PH_4I
0.731	16.53	12.09	...	Cd_2Hg
0.739	10.76	7.95	...	$Na_2(TiFe)Si_4O_{12}$, narsarsukite
0.742	8.85	6.57	$PbPb_2O_4$	$PbPb_2O_4$
0.752	9.74	7.32	...	Cu_2Pd
0.753	8.43	6.35	$H4_{17}$	$Ag_2SO_4.4NH_3$
0.757	15.63	11.83	S2$_2$	$Ca_{10}Mg_2Al_4Si_9O_{34}(OH)_4$, vesuvianite

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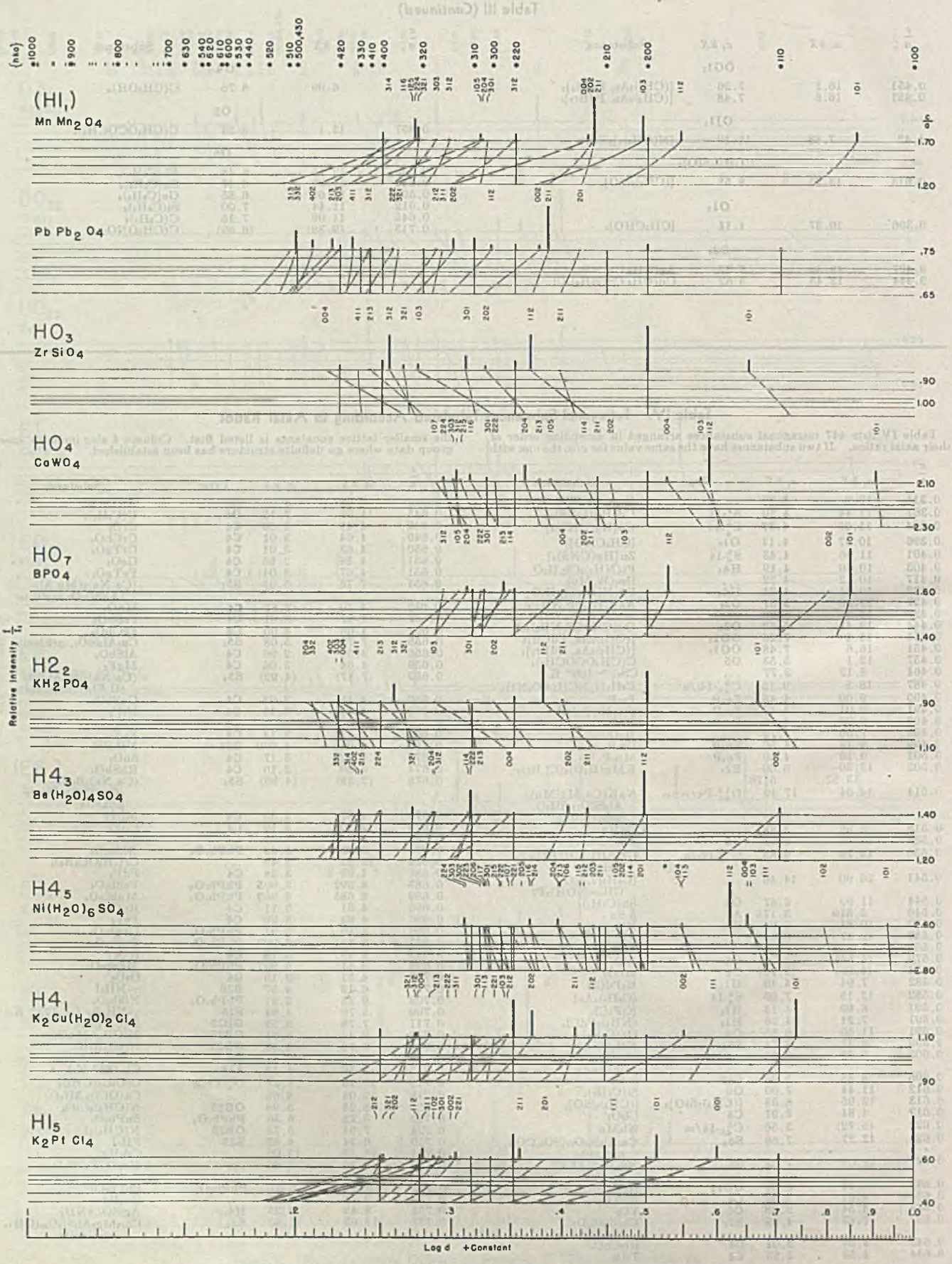

Figure 3. Representative Diffraction Patterns of Tetragonal Structures

Table IV (*Continued*)

c/a	a, kX	c, kX	Type	Substance
0.770	9.12	7.02	C^2_{4h}-$P4_2/m$	$C(COOCH_3)_4$
0.773	13.2	10.2	...	$LaAl_4$
0.780	10.45	8.14	...	$C_2(CH_3)_4Br_2$
0.784	8.87	6.95	...	$N(C_2H_5)_4I$
0.787	(4.79)	(3.77)	C4	TeO_2
0.803	9.29	7.46	C^3_{4h}-$P4/n$	PCl_5
0.806	6.052	4.878	C16	Al_2Cu
0.814	6.52	5.31	C16	Sn_2Fe
0.818	6.647	5.434	C16	Sn_2Mn
0.821	15.6	12.8	...	2-Hydroxy-10-methoxy-1,2,3,4,5,6,7,8,13,14,-15-dodecahydrochrysene
0.825	3.89	3.21	L10	NiZn
0.830	11.2	9.3	D^4_{2d}-$P\bar{4}2_1c$	$Si[SC(CH_3)_3]_4$
0.830	11.2	9.3	D^4_{2d}-$P\bar{4}2_1c$	$Ge[SC(CH_3)_3]_4$
0.830	11.2	9.3	D^4_{2d}-$P\bar{4}2_1c$	$Sn[SC(CH_3)_3]_4$
0.832	5.099	4.240	C16	Fe_2B
0.838	11.1	9.3	...	$(CH_3)_2CHS-Si[SC(CH_3)_3]_3$
0.841	5.006	4.212	C16	Co_2B
0.846	5.899	4.991	C16	Ge_2Fe
0.847	9.76	8.27	$NaBaPO_4$	$NaBaPO_4$
0.848	9.84	8.34	$NaBaPO_4$	$KBaPO_4$
0.851	4.980	4.236	C16	Ni_2B
0.852	6.835	5.821	C16	Pb_2Pd
0.857	6.348	5.441	C16	Sn_2Co
0.857	9.25	7.93	$NaBaPO_4$	$NaSrPO_4$
0.859	9.50	8.16	$NaBaPO_4$	$KSrPO_4$
0.867	7.13	6.18	HO_2	YVO_4
0.871	5.74	5.00	GO_9	NH_4NO_3-II (357–398° K.)
0.873	8.02	7.00	B37	TlSe
0.874	7.25	6.34	HO_3	$CaCrO_4$
0.880	(6.32)	(5.56)	($E6_2$)	$SrO_2.8H_2O$
0.880	6.651	5.853	C16	Pb_2Rh
0.880	(11.36)	(9.96)	...	Ag_2Ca
0.888	6.87	6.10	HO_3	YPO_4
0.895	4.96	4.44	...	~ZrH_2
0.901	6.58	5.93	HO_3	$ZrSiO_4$
0.904	6.13	5.54	D^7_{4h}-$P4/nmm$	$CuB_2O_4.CuCl_2.4H_2O$, bandylite
0.906	(6.41)	(5.81)	($E6_1$)	$Sr(OH)_2.8H_2O$
0.910	6.89	6.27	HO_3	$YAsO_4$
0.917	5.83	5.35	...	~$MnBi_2$
0.921	9.69	8.92	$F1_1$	$Hg(CN)_2$
0.930	4.85	4.51	...	$PbIn_{2-3}$
0.933	8.48	7.91	C^6_{4h}-$I4/m$	$AgClO_3$
0.934	10.58	9.88	...	$(Ca,Na)_3Be(Si,Al)_2-(O,F)_7$,meliphanite
0.935	3.98	3.72	L10	AuCu
0.936	3.774	3.533	A6	γ-Mn
0.936	7.61	7.12	$H2_2$	KH_2AsO_4
0.937	5.83	5.46	C^1_{4v}-$P4mm$	$2Pb(OH)_2.CuCl_2$, diaboleite
0.938	7.43	6.97	$H2_2$	KH_2PO_4
0.941	8.59	8.08	...	$AgBrO_3$
0.948	(3.85)	(3.65)	...	$W_{12}O_{32}(OH)_2$
0.952	3.76	3.58	A6	95Mn.5Cu
0.960	3.77	3.62	...	96Mn.4Pd
0.962	3.767	3.624	A6	89Mn.11Cu
0.962	4.18	4.02	...	~70Mo-30N
0.966	3.85	3.72	L10	FePd
0.967	3.66	3.54	L10	NiMn
0.971	4.20	4.08	...	62Mn.38N
0.974	8.12	7.91	$J1_{11}$	$AgSb(OH)_6$
0.975	8.00	7.80	...	*trans*-$Pd(NH_3)_2Cl_2$
0.976	3.77	3.68	...	92Mn.8N
0.977	8.7	8.5	...	$Pd(NH_3)_2I_2$
0.981	3.764	3.693	A6	79Mn.21Cu
0.984	8.01	7.88	$J1_{11}$	$NaSb(OH)_6$
0.986	(3.61)	3.56	...	Ni_4Mo
0.998	3.752	3.744	A6	66Mn.34Cu
1.00	6.34	6.34	($E3_1$)	Ag_2HgI_4
1.003	7.52	7.54	$H2_2$	$NH_4H_2PO_4$
1.005	7.70	7.74	$H2_2$	$NH_4H_2AsO_4$
1.01	3.99	4.02	$E2_1$	$BaTiO_3$
1.01	4.96	5.03	(L12)	$SrPb_3$
1.01	(6.08)	(6.14)	($E3_1$)	Cu_2HgI_4
1.02	5.07	5.16	...	ZrO_2 (<1273° K.)
1.02	6.29	6.42	C^1_4-P4	$Pt(NH_3)_4PtCl_4$
1.02	7.81	8.00	$H4_1$	$Rb_2CuCl_4.2H_2O$
1.03	6.37	6.58	B34	(Pd, Pt, Ni)S
1.04	5.79	6.00	...	~Ni_2Sb
1.04	6.35	6.60	B34	PdS
1.04	10.29	10.55	...	$Mg(ClO_2)_2.6H_2O$
1.04	10.64	11.07	D^{10}_4-$I4_12$	Cr_2Ni
1.05	7.58	7.96	$H4_1$	$(NH_4)_2CuCl_4.2H_2O$
1.05	7.9	8.3	$H4_1$	$(NH_4)_2CuBr_4.2H_2O$
1.05	12.95	13.65	C^6_{4h}-$I4_1/a$	$KAlSi_2O_6$, leucite
1.06	2.84	3.01	...	α-Martensite
1.06	3.89	4.13	($E2_1$)	$PbTiO_3$
1.06	7.45	7.88	$H4_1$	$K_2CuCl_4.2H_2O$
1.06	22.0	23.3	...	$Al_2C_{12}O_{12}.18H_2O$, mellite
1.08	4.585	4.937	A6	In
1.09	7.50	8.16	$H4_1$	$(NH_4)_2FeCl_4.2H_2O$
1.09	8.13	8.83	Phosgenite	$Pb_3Cl_2CO_3$
1.09	8.34	9.06	Phosgenite	$Pb_3Br_2CO_3$
1.13	6.70	7.60	K_3CrO_8	K_3CrO_8
1.13	7.37	8.34	K_3CrO_8	Cs_3TaO_8
1.14	(5.33)	(6.08)	...	$AgFO_3$
1.14	7.05	8.05	K_3CrO_8	Rb_3TaO_8
1.14	15.84	18.01	$J3_1$	$K_2TlCl_6.2H_2O$
1.15	6.27	7.22	C11	CsO_2
1.15	16.95	19.45	$J3_1$	$Rb_3TlBr_6.8/7H_2O$
1.16	5.99	7.02	C11	RbO_2
1.16	6.07	7.03	$F5_2$	KNCO
1.16	6.09	7.06	$F5_2$	KN_3
1.16	6.78	7.86	K_3CrO_8	K_3CbO_8
1.16	6.78	7.88	K_3CrO_8	K_3TaO_8
1.17	2.75	3.21	L10	NiZn
1.17	6.36	7.41	$F5_2$	RbN_3
1.18	5.70	6.73	C11	KO_2
1.20	...	...	C11	UC_2
1.20	4.28	5.13	OB21	CH_3NH_3Cl
1.20	5.67	6.81	$F5_2$	KFHF
1.21–1.31	4.05–3.98	4.90–5.10	D^7_{4h}-$P4/nmm$	$PbO-Bi_2O_3$
1.21	6.98	8.42	$H5_{10}$	$Ca(UO_2)_3(PO_4)_2.6-1/3H_2O$
1.22	3.55	4.33	B10	LiOH
1.25	6.99	8.75	$J1_8$	$K_2OsO_2Cl_4$
1.26	3.36	4.25	...	α-LiBi
1.26	3.98	5.01	B10	PbO
1.26	12.43	15.6	...	$Ca_4NaAl_2Si_4O_{16}$, sarcolite
1.27	3.80	4.81	B10	SnO
1.28	(4.14)	(5.28)	C11	ThC_2
1.28	8.81	11.27	...	$C_2(CH_3)_2Br_4$
1.28	11.70	14.95	...	$Fe_2(TeO_3)_3.xH_2O$, mackayite
1.29	8.97	11.55	D^2_{4h}-$P4/mcc$	$Sr(OH)_2.8H_2O$
1.32	2.609	3.533	A6	γ-Mn
1.32	2.78	3.66	...	Ni-N
1.32	2.81	3.72	L10	AuCu
1.32	7.22	9.53	...	C_4H_4S (~100° K.), thiophene
1.33	4.73	6.29	...	$5PbCrO_4.3PbMoO_4.-10PbSO_4$
1.35	2.66	3.58	A6	95Mn.5Cu
1.35	3.24	4.38	NaBi	MgIn
1.35	7.38	9.96	...	$(Ca,Na)_3BeSi_2(O,OH,F)_7$, leucophanite
1.36	2.66	3.62	A6	89Mn.11Cu
1.36	7.57	10.28	D^{19}_{4h}-$I4/amd$	$Ba(CH_3COO)_2$
1.37	2.59	3.54	L10	NiMn
1.37	2.72	3.72	L10	FePd
1.39	2.66	3.69	A6	79Mn.21Cu
1.39	3.46	4.80	NaBi	NaBi
1.40	4.96	6.92	C30	SiO_2
1.40	8.75	12.28	$D5_9$	Cd_3P_2
1.41	2.65	3.74	A6	66Mn.34Cu
1.41	5.00	7.06	C30	$AlPO_4$
1.41	5.48	7.74	...	Li_2O_2
1.41	8.10	11.39	...	Ni_3Sb_4
1.41	8.10	11.45	$D5_9$	Zn_3P_2
1.41	8.32	11.76	$D5_9$	Zn_3As_2
1.41	8.95	12.65	$D5_9$	Cd_3As_2
1.42	7.88	11.19	$OJ1_1$	$[N(CH_3)_4]_2SiF_6$
1.43	12.83	18.38	D^6_{4h}-$P4/mnc$	$B_2O_3.24WO_3.66H_2O$
1.43	12.98	18.52	...	$H_4SiW_{12}O_{40}.31H_2O$
1.44	6.09	8.76	$O4_{12}$	$C(CH_2OH)_4$
1.44	12.80	18.40	...	$(NH_4)_3BW_{12}O_{40}.26H_2O$
1.45	7.49	10.87	$K7_6$	$Cs_2AuAuCl_6$
1.45	9.50	13.81	D^1_{4h}-$P4/mmm$	$CuCl.3SC(NH_2)_2$
1.46	5.548	8.093	DO_{22}	$TiGa_3$
1.46	(7.74)	(11.31)	HO_7	$Y(Cb, Ta)O_4$
1.46	(7.76)	(11.32)	HO_7	$YCbO_4$
1.47	3.77	5.52	B10	FeSe
1.47	(7.75)	(11.41)	HO_7	$YTaO_4$
1.48	5.85	8.68	($H1_1$)	$CuFe_2O_4$
1.48	7.01	10.36	$K7_8$	$Na_5Al_3F_{14}$
1.49	6.65	9.91	...	Na_2O_2
1.49	7.38	11.01	$K7_6$	$Cs_2AgAuCl_6$
1.50	6.97	10.43	$J1_9$	$AgCo(NH_3)_2(NO_2)_4$
1.51	4.14	6.25	...	$Pb(ClO_2)_2$
1.51	4.85	7.33	OB21	$C_2H_7NH_3I$
1.52	3.24	4.94	A6	In
1.52	4.459	6.796	HO_7	$BAsO_4$
1.53	3.992	6.091	C38	Cu_2Sb
1.53	4.332	6.640	HO_7	BPO_4
1.55	5.605	8.712	DO_{22}	$ZrGa_3$
1.56	5.334	8.305	DO_{22}	VAl_3
1.56	9.07	14.12	C^6_{4v}-$P4cc$	$[N(CH_3)_2(C_2H_5)_2]_2SnCl_6$
1.57	5.17	8.12	...	~Fe_2Ti
1.57	5.422	8.536	DO_{22}	$TaAl_3$
1.58	4.48	7.10	OB21	$C_2H_7NH_3Cl$
1.58	5.425	8.579	DO_{22}	$TiAl_3$
1.58	5.427	8.584	DO_{22}	$CbAl_3$
1.58	6.20	9.82	($H1_1$)	$CaIn_2O_4$
1.58	9.18	14.47	$K3_1$	Cs_2CoCl_5
1.59	5.74	9.15	($H1_1$)	$ZnMn_2O_4$
1.61	4.08	6.56	C38	Mn_2Sb
1.61	4.39	7.05	C11	BaC_2
1.61	4.57	7.36	OB21	$C_2H_7NH_3Br$
1.63	6.12	9.87	($H1_1$)	$CdIn_2O_4$
1.61	8.7	14.0	$K3_1$	Rb_2CoCl_5
1.61	4.11	6.68	C11	SrC_2
1.63	15.0	24.4	D^{17}_{4h}-$I4/mmm$	~$PbCl_2.Cu(OH)_2$, cumengeite
1.64	5.75	9.42	($H1_1$)	$MnMn_2O_4$
1.65	3.627	5.973	C38	Fe_2As

(*Continued on page 93*)

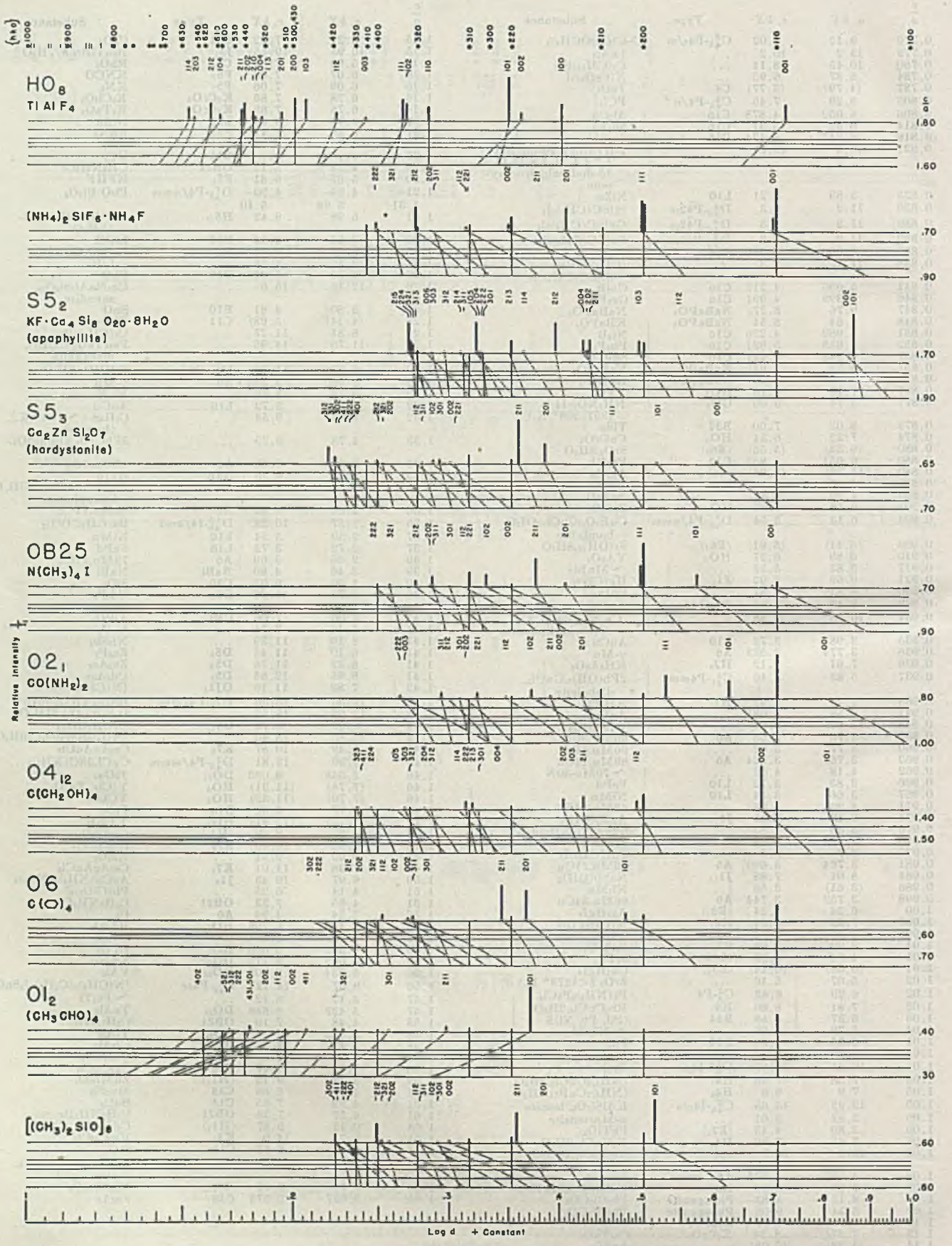

Figure 4. Representative Diffraction Patterns of Tetragonal Structures

Table IV (*Continued*)

$\frac{c}{a}$	a, kX	c, kX	Type	Substance
1.65	3.82	6.30	C11	NdC_2
1.65	3.87	6.37	C11	CaC_2
1.65	4.38	7.22	EO_1	BaFCl
1.66	3.85	6.38	C11	PrC_2
1.67	3.54	5.91	C11	CaO_2
1.67	3.75	6.28	C11	SmC_2
1.67	3.76	6.27	C38	Mn_2As
1.67	3.87	6.48	C11	CeC_2
1.67	3.92	6.55	C11	LaC_2
1.68	4.10	6.88	EO_1	SrFCl
1.68	9.93	16.70	...	l-$Co(NH_3.CH_2.CH_2.NH_3)_2Br_2.H_2O$
1.69	5.83	9.88	D_{4h}^{19}-I4/*amd*	$6CuO.Cu_2O$, paramelaconite
1.71	4.65	7.93	EO_1	BAFI
1.71	8.39	14.34	$K3_4$	$NH_4Pb_2Br_5$
1.72	5.09	8.76	OB20	CH_2NH_2Br
1.72	8.41	14.5	$K3_4$	$RbPb_2Br_5$
1.73	3.55	6.14	HO_8	$KAlF_4$
1.73	3.62	6.26	HO_8	$RbAlF_4$
1.73	8.14	14.1	$K3_4$	KPb_2Br_5
1.74	3.03	5.26	B17	PdO
1.75	3.613	6.333	C38	Cr_2As
1.75	5.11	8.96	OB20	CH_2NH_2I
1.76	3.03	5.32	B17	PtO
1.76	3.47	6.10	B17	PtS
1.76	3.61	6.37	HO_8	$TlAlF_4$
1.76	3.89	6.83	EO_1	CaFCl
1.76	4.09	7.21	EO_1	PbFCl
1.76	9.00	15.84	$S5_2$	$KCa_4Si_8O_{20}F.8H_2O$, apophyllite
1.77	3.59	6.35	HO_8	NH_4AlF_4
1.79	3.78	6.77	C11	BaO_2
1.79	14.38	25.80	D_4^{10}-I4$_1$2	$KUO_2(CH_3COO)_3$
1.81	5.72	10.37	...	α-$Pt(NH_3)_2Cl_4$
1.82	4.18	7.59	EO_1	PbFBr
1.82	5.66	10.30	$E1_1$	$AgFeS_2$
1.83	4.16	7.61	D_{4h}^{10}-P4/*mcm*	NH_4CN
1.84	10.7	19.7	...	$(C_2H_5)_3As.AgI$
1.85	3.55	6.55	C11	SrO_2
1.89	3.89	7.37	EO_1	BiOCl
1.89	4.19	7.94	$E2_5$	NH_4HgCl_3
1.90	2.69	5.10	...	$FeSi_2$
1.94	4.70	9.10	$FeTa_2O_6$	$NiTa_2O_6$
1.94	4.71	9.12	$FeTa_2O_6$	$Fe(Cb,Ta)_2O_6$, mossite
1.94	4.73	9.16	$FeTa_2O_6$	$CoTa_2O_6$
1.95	4.70	9.18	$FeTa_2O_6$	$MgTa_2O_6$
1.95	4.71	9.18	$FeTa_2O_6$	$FeTa_2O_6$, tapiolite
1.95	7.80	15.23	...	$Pb(Cl,OH)_24PbO.2Fe_2O_3$, hämatophanite
1.97	(4.28)	(8.42)	C11	KHC$_2$
1.97	5.26	10.37	$E1_1$	$CuFeS_2$, chalcopyrite
1.97	5.46	10.73	$H2_8$	Cu_2FeSnS_4, stannite
1.98	13.99	27.70	D_4^{10}-I4$_1$2	$KUO_2(CH_3COO)_3$
1.99	4.02	8.02	...	H_2O_2
1.99	9.50	18.93	D_{4h}^{20}-I4/*acd*	$3Mn_2O_3.MnSiO_3$, braunite
2.00	13.79	27.60	D_4^{10}-I4$_1$2	$NH_4UO_2(CH_3COO)_3$
2.03	15.4	31.2	...	$Pb_3Cu_4Cl_{10}O_4.6H_2O$, pseudoboleite
2.06	2.83	5.82	...	$\sim CuGa_2$
2.06	3.92	8.09	DO_{22}	$TiGa_3$
2.07	3.92	8.11	EO_1	BiOBr
2.08	5.42	11.3	D_{2d}^{12}-I$\bar{4}$2d	$(Bi,W)_8$-nO_{12}, russellite
2.10	(3.89)	(8.17)	C11	NaHC$_2$
2.14	7.50	16.05	D_{4h}^{6}-P4/*ncc*	$BaFeSi_4O_{10}$, gillespite
2.15	5.94	12.80	HO_4	NH_4IO_4
2.16	12.98	28.10	$O4_{11}$	$AgUO_2(CH_3COO)_3.xH_2O$
2.17	5.15	11.17	HO_4	$CdMoO_4$
2.17	5.24	11.38	HO_4	$CaWO_4$
2.17	5.35	11.63	HO_4	$NaLa(WO_4)_2$
2.18	5.32	11.59	HO_4	$NaCe(WO_4)_2$
2.18	5.32	11.60	$La_2(MoO_4)_3$	$Pr_2(MoO_4)_3$
2.18	5.34	11.63	HO_4	$LiLa(WO_4)_2$
2.19	5.23	11.44	HO_4	$CaMoO_4$
2.19	5.27	11.55	HO_4	$NaBi(MoO_4)_2$
2.19	5.29	11.58	$La_2(MoO_4)_3$	$Nd_2(MoO_4)_3$
2.19	5.36	11.72	HO_4	$NaReO_4$
2.20	3.77	8.31	DO_{22}	VAl_3
2.20	3.96	8.71	DO_{22}	$ZrGa_3$
2.20	5.23	11.50	HO_4	$LiBi(MoO_4)_2$
2.20	5.31	11.67	HO_4	$LiLa(MoO_4)_2$
2.20	5.33	11.70	HO_4	$NaLa(MoO_4)_2$
2.20	5.40	11.90	HO_4	$SrWO_4$
2.20	5.75	12.63	HO_4	KIO_4
2.20	5.87	12.94	HO_4	$RbIO_4$
2.20	5.87	12.94	HO_4	NH_4ReO_4
2.21	5.33	11.78	$La_2(MoO_4)_3$	$Ce_2(MoO_4)_3$
2.21	5.35	11.84	$La_2(MoO_4)_3$	$La_2(MoO_4)_3$
2.21	5.44	12.01	HO_4	$PbWO_4$
2.21	5.44	12.03	HO_4	$KLa(WO_4)_2$
2.22	5.38	11.92	HO_4	$KBi(MoO_4)_2$
2.22	5.39	11.94	HO_4	$KCe(WO_4)_2$
2.22	5.62	12.50	HO_4	$KReO_4$
2.23	3.83	8.54	DO_{22}	$TaAl_3$
2.23	5.22	11.62	$La_2(MoO_4)_3$	$Sn_2(MoO_4)_3$
2.23	5.35	11.92	HO_4	$AgReO_4$
2.23	5.37	11.96	HO_4	$SrMoO_4$
2.23	5.41	12.08	HO_4	$PbMoO_4$
2.23	5.42	12.11	HO_4	$KLa(MoO_4)_2$
2.24	3.836	8.579	DO_{23}	$TiAl_3$
2.24	3.837	8.584	DO_{23}	$CbAl_3$
2.24	5.32	11.93	HO_4	$NaIO_4$
2.24	5.37	12.01	HO_4	$AgIO_4$
2.26	5.62	12.70	HO_4	$BaWO_4$
2.27	5.80	13.17	HO_4	$RbReO_4$
2.28	4.01	9.14	EO_1	BiOI
2.29	5.56	12.76	HO_4	$BaMoO_4$
2.30	5.08	11.69	HO_4	$BiAsO_4$
2.31	5.76	13.33	HO_4	β-$TlReO_4$ (400° K.)
2.32	5.65	13.08	HO_4	$KOsO_3N$
2.36	4.92	11.62	$D3_1$	Hg_2I_2
2.36	5.46	12.89	HO_4	$KCrO_3F$
2.36	10.09	23.85	...	$C_{28}H_{26}N_4$, acetonylpyrol
2.39	4.65	11.10	$D3_1$	Hg_2Br_2
2.40	10.0	24.0	D_{4h}^{19}-I4/*amd*	*cis*-$[Pt(NH_3)(C_2H_4)Cl_2]$
2.42	12.5	30.25	...	$6Pb(S,Tl)_2.AuTl_3$, nagyagite
2.44	4.46	10.89	$D3_1$	Hg_2Cl_2
2.45	3.21	7.88	C20	WSi_2
2.46	3.20	7.86	C20	$MoSi_2$
2.46	4.53	11.14	$D1_1$	Al_4Ba
2.47	6.29	15.55	...	$(CH_2CO)_2NI$
2.48	4.45	11.04	$D1_1$	Al_4Sr
2.51	3.75	9.43	C5	TiO_2
2.52	5.61	14.13	HO_4	$CsSO_3F$
2.53	5.72	14.50	HO_4	$CsCrO_3F$
2.54	4.35	11.07	$D1_1$	Al_4Ca
2.68	7.04	18.88	...	$CaNa_4Al_{12}(PO_4)_8(OH)_{16}.6H_2O$, wardite
2.80	6.40	17.95	D_4^3-P4$_1$2	$C_5H_4O_4N_4$, l-spiro-5,5'-dihydantoin
2.80	6.95	19.45	...	$[(NH_2)_2CNH]_3.H_2CO_3$
2.81	4.78	13.43	$Tl(CH_3)_2I$	$Tl(CH_3)_2I$
2.82	7.03	19.8	...	$2,4,6(C_6H_2)I(NO_2)_3$
2.82	7.25	20.47	...	$C_6H_4[1,2](COC_2H_3)_2$
2.83	4.36	12.36	C13	HgI_2
2.88	2.998	8.630	C48	Cr_2Al
2.91	7.05	20.5	D_{4h}^{17}-I4/*mmm*	$Cu(UO_2)_2(PO_4)_2.8H_2O$ torberite
2.95	6.99	20.63	$H5_8$	$Ca(UO_2)_2(PO_4)_2.10^1/_2H_2O$
2.95	5.18	15.3	OB20	$C_6H_9NH_3I$
2.96	5.02	14.85	OB20	$C_6H_9NH_3Cl$
2.98	3.66	10.9	$D3_1$	Hg_2F_2
3.02	5.96	17.99	...	$C_2H_4(NH_2)_2.H_2SO_4$
3.03	5.02	15.23	OB20	$C_6H_9NH_3Br$
3.08	4.47	13.78	$Tl(CH_3)_2I$	$Tl(CH_3)_2Br$
3.13	3.840	12.03	D_{4h}^{17}-I4/*mmm*	$LiBi_2O_4Cl_2$
3.13	3.877	12.13	$LiBi_2O_4Cl_2$	$NaBi_2O_4Cl_2$
3.16	5.513	17.422	...	$MnSi_2$
3.20	3.925	12.55	$LiBi_2O_4Cl_2$	$NaBi_2O_4Br_2$
3.20	3.943	12.62	$LiBi_2O_4Cl_2$	$Cd_2Bi_2O_4Br_2$
3.22	3.876	12.47	$LiBi_2O_4Cl_2$	$LiBi_2O_4Br_2$
3.27	4.29	14.02	$Tl(CH_3)_2I$	$Tl(CH_3)_2Cl$
3.33	5.01	16.70	OB20	$C_6H_{11}NH_3Cl$
3.34	3.97	13.24	$LiBi_2O_4Cl_2$	$Cd_2Bi_2O_4I_2$
3.34	3.990	13.31	$LiBi_2O_4Cl_2$	$NaBi_2O_4I_2$
3.35	3.941	13.19	$LiBi_2O_4Cl_2$	$LiBi_2O_4I_2$
3.35	5.16	17.3	OB20	$C_6H_{11}NH_3I$
3.40	5.00	17.0	OB20	$C_6H_{11}NH_3Br$
3.47	4.13	14.35	D_{4h}^{19}-I4/*amd*	$ThSi_2$
3.68	5.07	18.65	ZnP_2	ZnP_2
3.73	5.28	19.70	ZnP_2	CdP_2
3.78	5.16	19.50	OB20	$C_6H_{13}NH_3I$
3.91	4.09	15.99	...	La_2MoO_6
3.93	4.98	19.55	OB20	$C_6H_{13}NH_3Cl$
4.02	4.93	19.8	OB20	$C_6H_{13}NH_3Br$
4.03	15.4	62.0	...	$Pb_8Cu_3Ag_2Cl_{21}O_8.9H_2O$, boleite
4.15	5.18	21.5	OB20	$C_7H_{15}NH_3I$
4.25	4.96	21.1	OB20	$C_7H_{15}NH_3Cl$
4.32	4.003	17.29	DO_{21}	$ZrAl_3$
4.58	5.18	23.7	OB20	$C_8H_{17}NH_3I$
4.59	7.32	33.6	D_4^4-P4$_1$2$_1$	β-methyl d-glucoside
5.42	5.18	28.1	OB20	$C_{10}H_{21}NH_3I$
5.76	3.78	21.77	...	Beyerite
5.88	5.18	30.46	OB20	$C_{11}H_{23}NH_3I$
6.03	5.18	31.24	OB20	$C_{12}H_{25}NH_3I$
6.74	5.7	38.4	...	$C_{14}H_8O_2[2,7](NO_2)_2$, 2,7-dinitroanthraquinone

[End of article on Diffraction Data]

Application of Colorimetry to the Analysis of Corrosion-Resistant Steels

Photometric Determination of Copper

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Photometric measurement of the cuprammonium ion, $Cu(NH_3)_4^{++}$, is best made at 580 millimicrons, where the effects of ammonia concentration and other ions that may be present are negligible. Interference at 620 millimicrons, the region of maximum sensitivity, is significant. A rapid procedure, applicable to low-alloy and corrosion-resistant steels, is given and data are presented in support of the validity of the method.

DURING an investigation of methods for the determination of low percentages of residual elements in corrosion-resistant steels (*1*, *2*, *10*, *14*), a rapid photometric determination of copper was developed which is more easily adapted to routine use than the usual gravimetric α-benzoinoxime procedure (*6*) or that in which copper is separated as thiocyanate and titrated iodometrically (*7*).

The colorimetric determination of copper by conversion to the cuprammonium ion, $Cu(NH_3)_4^{++}$, has been used for a number of years (*5*, *13*, *15*). The principal objection to the method is that the color is a function of the ammonia concentration which, because of the volatile nature of the reagent, is not always easily controlled.

Mehlig, in the analysis of copper ores (*8*), has overcome the difficulty by destroying the color of the ammine with cyanide, estimating the copper by the difference in spectrophotometric transmission before and after the cyanide addition. Yoe and Barton (*16*) suggest the use of less volatile triethanolamine for the photoelectric measurement of the cuprammonium color. Among organic reagents suggested for the colorimetric determination of copper, sodium diethyldithiocarbamate (*3*), dithizone (*4*), and 1,10-phenanthroline (*11*) have been found applicable.

It was believed, however, that the full possibilities of the use of ammonia for the photometric determination of copper had not been explored and an investigation of conditions was begun.

SPECTROPHOTOMETRIC INVESTIGATION

In spectrophotometric studies previously made (*9*, *16*) it has been found that both absorption by the copper-ammonia complex and wave length of maximum absorption increase with the ammonia concentration. At the usual concentration of about 3 *N*, maximum absorption is at 620 millimicrons. From one of these studies (*16*), however, it was observed that the transmissions of two solutions containing 100 p.p.m. of copper with ammonia concentrations of 0.4 *M* and 2.5 *M*, respectively, coincided at about 560 millimicrons. From this it appeared that if there were a spectral band at which the ammonia concentration had a negligible effect, the absorption of the copper-ammonia complex at such a wave length could be conveniently utilized for the accurate photometric determination of copper. Accordingly, four solutions were prepared, each containing 2 mg. of copper (as the sulfate) and an excess of ammonium hydroxide (0.90 specific gravity) varying from 5 to 20 ml. The solutions were diluted to 100 ml. in flasks which were stoppered to prevent escape of ammonia, then rapidly transferred to absorption cells and transmissions immediately measured by a General Electric recording spectrophotometer set for a spectral band width of 10 millimicrons. The curves obtained (Figure 1) intersected at approximately 580 millimicrons, but, in agreement with the results of the previous investigations, there were considerable differences in the region of maximum absorption. The spectrophotometric transmission measurement was repeated for two series of solutions containing 5 and 10 mg. of copper, respectively, with analogous results (Figure 1).

The absorptions of the solutions were then measured with a Klett-Summerson photoelectric colorimeter, using a filter with maximum transmission at 580 millimicrons and a 4-cm. glass absorption cell. The galvanometer scale readings, which are logarithmic on this instrument, were found to be almost directly proportional to the copper content. The difference in colorimeter readings between solutions containing the same amount of copper but different ammonia concentrations was negligible. Measurement of the same solutions using a filter with maximum transmission at 620 millimicrons, however, gave readings which decreased proportionately with a decrease in ammonia concentration; a solution containing the equivalent of 0.20% of copper with a 20-ml. excess showed only 0.16% present with a 5-ml. excess.

Müller (*12*) found that Beer's law holds for the copper-ammonia complex up to concentrations of about 1 gram of copper per liter, using a filter transmitting in the region of maximum sensitivity. The author's series of measurements at 580 millimicrons, however, shows the curve of concentration *vs.* log transmission to deviate slightly from linearity at concentrations above 60 mg. per liter.

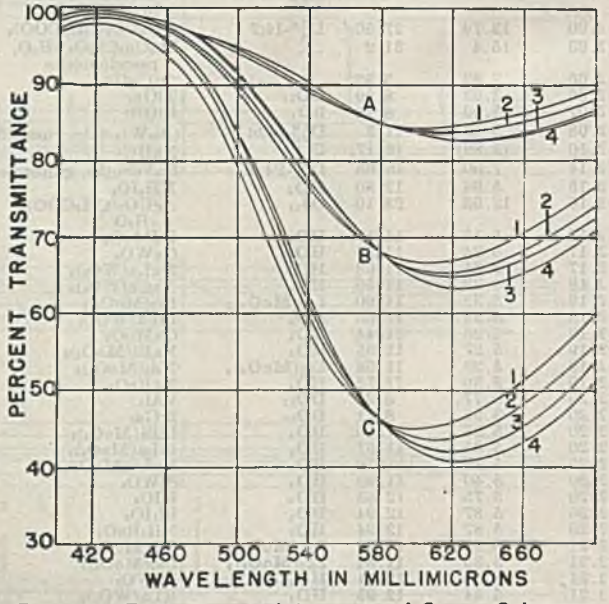

Figure 1. Transmittance of Ammoniacal Copper Solutions (4-Cm. Cell)

Se No.	Copper Concentration *Mg./100 ml.*	Curve No.	NH_4OH Excess *Ml.*
A	2	1	5
B	5	2	10
C	10	3	15
		4	20

Table I. Determination of Copper in Steel

Sample	Type of Steel	Copper Present %	Copper Found %
N.B.S. 19d	Plain carbon	0.158	0.16
N.B.S. 34a	Plain carbon	0.222	0.22
N.B.S. 35a	Plain carbon	0.267	0.27
N.B.S. 73a	14% Cr	0.080	0.08
N.B.S. 101b	18% Cr–9% Ni	0.16[a]	0.16
N.B.S. 121a	18% Cr–10% Ni 0.4% Ti	0.08[a]	0.06
N.B.S. 133	14% Cr–0.66% Mo	0.061	0.06
Lab. No. T-1757	20% Cr–10% Ni 4.1% Mn, 0.22% Co	0.30[b]	0.31
Lab. No. T-2284	27% Cr–22% Ni 1.8% Mn	0.13[b]	0.13
Lab. No. T-2285	21% Cr–11% Ni 4.6% Mn, 0.23% Cb	0.25[b]	0.25

[a] Provisional value.
[b] Determined by CuCNS–$Na_2S_2O_3$-KI titration method.

PRELIMINARY SEPARATION

It was found that the necessary preliminary separation of the copper is most rapidly and conveniently made by precipitating as the sulfide with thiosulfate (*7*). The copper precipitate is ordinarily accompanied by some iron, manganese, and free sulfur. Silica may also separate out during the dissolution of the sample, but can easily be eliminated by a few drops of hydrofluoric acid. Iron is precipitated upon the subsequent addition of ammonia and may be filtered off prior to the colorimetric estimation. Free sulfur and small amounts of manganese are removed with the iron; larger quantities of manganese, that may be coprecipitated with the copper sulfide from special steels containing as high as 4 or 5% of this element, frequently escape immediate precipitation with the ammonia but come down slowly upon standing. In this case, quantitative separation may be made by the addition of an oxidant, such as ammonium persulfate, to the ammoniacal solution.

In the proposed method, the impure copper sulfide precipitate is returned to the original flask after filtration and decomposed by the use of a mixture of nitric and perchloric acids, instead of being ignited to mixed oxides and redissolved in nitric acid. Perchlorates do not interfere with the copper-ammonia color (*9*); however, a minimum of perchloric acid is used to avoid formation of slightly soluble ammonium perchlorate crystals. The dissolution of corrosion-resistant steels, especially those of the 25% Cr–20% Ni types, frequently proceeds slowly in sulfuric acid alone. Accordingly, a mixture of hydrochloric and sulfuric acids is used to dissolve the sample.

APPARATUS AND REAGENTS

Klett-Summerson Photoelectric Colorimeter, Research model.

4-Cm. Glass Absorption Cell.

Glass Filter, transmission maximum at 580 millimicrons.

Solvent Acid Mixture. Add 250 ml. of concentrated hydrochloric acid to a mixture of 600 ml. of water and 150 ml. of concentrated sulfuric acid.

Sodium Thiosulfate Solution, 50%. Dissolve 500 grams of sodium thiosulfate in 500 ml. of water.

Nitric-Perchloric Acid Mixture. Mix 250 ml. of concentrated nitric acid and 80 ml. of perchloric acid (70 to 72%).

Ammonium Nitrate Solution, 1%. Dissolve 10 grams of ammonium nitrate in 1 liter of water.

PROCEDURE

Transfer 5 grams of sample to a covered 500-ml. Erlenmeyer flask and dissolve by warming gently with 100 ml. of solvent acid mixture. When dissolution is complete, remove the cover glass, add a few drops of hydrofluoric acid (48%), and boil for several minutes. Dilute to about 300 ml., heat to gentle boiling, and carefully add 20 ml. of sodium thiosulfate solution in 3- to 5-ml. increments. Continue the boiling until the precipitate is well coagulated (usually 15 to 20 minutes). Decant the hot solution through a coarse filter, rinse, and wash well with hot water.

Return the paper and precipitate to the original flask and add 35 ml. of nitric-perchloric acid mixture. Swirl the flask until the contents are thoroughly moistened by the acid mixture. Heat at a moderate temperature until the paper is decomposed and the sulfides are oxidized to yellow beads of free sulfur. Continue the digestion until dense fumes of perchloric acid are evolved, then allow to cool.

Add 35 ml. of water, neutralize with ammonium hydroxide, and add an excess of 2 to 3 ml. Heat to boiling. (If the steel is known to contain more than 1% of manganese, use an excess of 10 ml. of ammonium hydroxide, and add 2 grams of ammonium persulfate crystals to the boiling solution.) Continue the boiling for a minute or two, testing with a piece of litmus paper to ensure that the solution is still ammoniacal. Allow to cool to room temperature and filter through a coarse filter paper into a 100-ml. volumetric flask. Add 20 ml. of ammonium hydroxide to the filtrate. Rinse and wash with ammonium nitrate solution until the level in the flask just reaches the mark. Stopper, and mix well.

Set the zero point of the colorimeter with diluted ammonium hydroxide (1 to 4). Transfer a portion of the unknown solution to the absorption cell and obtain the colorimeter reading. Convert to percentage of copper by reference to a calibration curve prepared for the instrument by the use of portions of a standard copper nitrate solution.

ACCURACY AND PRECISION

Application of the method to the determination of copper in National Bureau of Standards and laboratory standard samples gave the results shown in Table I. The accuracy is comparable to that of other commonly used procedures. The precision of the method is good; the average deviations for N.B.S. samples 73a and 101b were about 0.002%.

CONCLUSION

The method is rapid—a set of 12 determinations can be completed in 2 hours after the samples have been dissolved. The speed of dissolution varies with the alloy composition and fineness of the sample; from 1 to 3 hours are required for corrosion-resistant steels, less for slightly alloyed steels.

Interference by other elements is negligible. Experiments have shown that in the analysis of corrosion-resistant steels no chromium or nickel is coprecipitated with the copper sulfide even when the amounts present run as high as 25% of each. However, small amounts of chromium, in the form of undecomposed carbides, may accompany the copper sulfide from special corrosion-resistant steels of high carbon content. The subsequent fuming with perchloric acid partially decomposes these carbides and oxidizes the chromium to chromic acid which passes into the filtrate with the copper-ammine. The author found that an ammoniacal copper solution containing 1000 parts of chromium (as chromate) per million showed an error of less than 0.002%—within the precision of the method. If desired, however, this slight interference may be completely eliminated by reducing the chromium with a few drops of hydrogen peroxide after the fuming with perchloric acid and removing as the insoluble hydroxide with the iron.

Although molybdate is included by Mehlig in a list of interfering anions (*9*), there was no measurable increase in absorption at 580 millimicrons upon the addition of 0.075 gram of molybdic acid (MoO_3) to several of the test solutions. This quantity of molybdate is equivalent to that formed from a steel containing 1% of molybdenum, assuming 100% coprecipitation of molybdenum with the copper.

Tungsten is occasionally present in corrosion-resistant steels in low residual amounts. It is, for the most part, removed during the course of the analysis; traces that may remain do not cause significant interference.

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Colorimetric Determination of Nitrites

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A General Electric recording spectrophotometer and a Beckman spectrophotometer were used to determine the effect of reagent concentration, order of addition of reagents, pH, temperature, light, nitrite concentration, and the presence of 68 diverse ions on the reddish purple coloration produced by 4-aminobenzenesulfonic acid (sulfanilic acid) and 1-aminonaphthalene (α-naphthylamine) in the presence of nitrous acid. Reliable determinations can be made in the range of 0.025 to 0.600 p.p.m. of nitrite ion in a 2-cm. cell. As little as 0.0005 p.p.m. of nitrite nitrogen can be determined by the use of 24-cm. Nessler tubes. Time must be allowed for complete diazotization before the coupling agent is added. Diazotization is carried out in strongly acidic solution at room temperature in diffuse light, and the system is buffered to pH 2.0 to 2.5 for coupling.

FOR decades small amounts of nitrite have been determined colorimetrically. This determination usually depends upon diazotization and coupling reactions. Nitrites react with primary aromatic amines in acidic solutions with the formation of diazonium salts which will couple with certain compounds to form intensely colored azo dyes.

Many procedures have been given for the diazotization of 4-aminobenzenesulfonic acid (sulfanilic acid) and coupling with 1-aminonaphthalene (α-naphthylamine) (*1*, *2*, *10*, *13*). Wallace and Neave (*18*) proposed the use of *N*,*N*-dimethyl-1-aminonaphthalene as the coupling agent. This has been used by some (*5*, *6*). Bratton and Marshall (*3*) investigated new coupling agents for diazotized 4-aminobenzenesulfonamide (sulfanilamide) and found *N*-(1-naphthyl)-ethylenediamine dihydrochloride most satisfactory. Shinn (*15*) and Kershaw and Chamberlain (*9*) made use of 4-aminobenzenesulfonamide and this coupling agent for the determination of nitrites.

This paper embodies the results of an investigation of the use of 4-aminobenzenesulfonic acid and 1-aminonaphthalene which is recommended by the American Public Health Association (*1*). The present investigation was undertaken to determine the sources of error in the method still officially recognized.

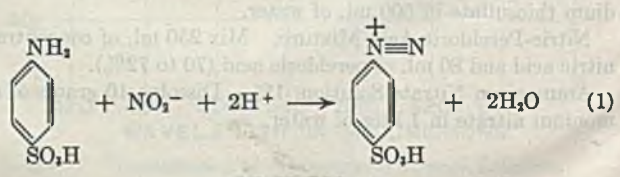
EXPERIMENTAL WORK

APPARATUS AND SOLUTIONS. Transmittancy measurements were made with a General Electric recording spectrophotometer operating with a spectral band width of 10 mμ, and with a Beckman spectrophotometer operating with a band width of approximately 1 mμ. Equivalent amounts of reagents were added to distilled water in the reference cell. All pH determinations were made with a glass electrode pH meter.

To prepare a stock solution of sodium nitrite (*14*) a solution containing about 1 gram of the salt in 100 ml. was aliquoted and analyzed by titration with potassium permanganate according to the U.S.P. method (*17*). An accurately known solution containing 5 p.p.m. of nitrite ion was prepared by suitable dilution of an aliquot. This solution is stable when protected from bacteria and carbon dioxide of the air. The use of boiled water helps eliminate both bacteria and carbon dioxide. One milliliter of chloroform per liter can be added to prevent bacterial growth and does not interfere with the color reaction. One-tenth gram or less of sodium hydroxide per liter may be added to prevent the liberation of the unstable nitrous acid by carbon dioxide of the air. The solution should have a pH of 8 to 11.5.

For this investigation a solution of 4-aminobenzenesulfonic acid was prepared by dissolving 0.60 gram of recrystallized material in 100 ml. of distilled water. Heating aids dissolution. The 1-aminonaphthalene hydrochloride solution was prepared by dissolving 0.60 gram of recrystallized material in 100 ml. of distilled water. The 4-aminobenzenesulfonic acid and the 1-aminonaphthalene hydrochloride are colorless solids when pure, but, especially the latter, tend to discolor on exposure to light and air. Discolored reagents should be recrystallized. The 4-aminobenzenesulfonic acid can be recrystallized from hot water. To recrystallize from 5 to 10 grams of 1-aminonaphthalene hydrochloride, add 2 grams of decolorizing charcoal (Norite) and 100 ml. of water and boil for a few minutes. Rapidly filter the hot mixture through a Büchner funnel fitted with a filter paper. If the filtrate is not clear and colorless, add another 2 grams of decolorizing charcoal, boil again, and refilter. Then add 25 ml. of concentrated hydrochloric acid to the filtrate and cool to 0° C. in an ice bath. Filter off the recrystallized hydrochloride on a Büchner funnel, air-dry the product on a porous plate in a dark place, and store it in a tightly closed, dark bottle. Hydrochloric acid solutions of this reagent show much less tendency to discolor than acetic acid solutions which are used by some.

COLOR REACTION. The color formed by 1-aminonaphthalene with diazotized 4-aminobenzenesulfonic acid is a reddish purple which has its minimum transmittancy near 520 mμ (Figure 1). The reactions involved may be indicated by the following equations:



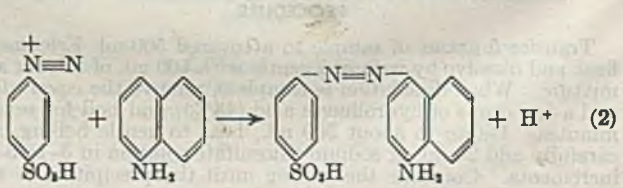


Table I. Effect of pH on Reaction Rates at 30° C.

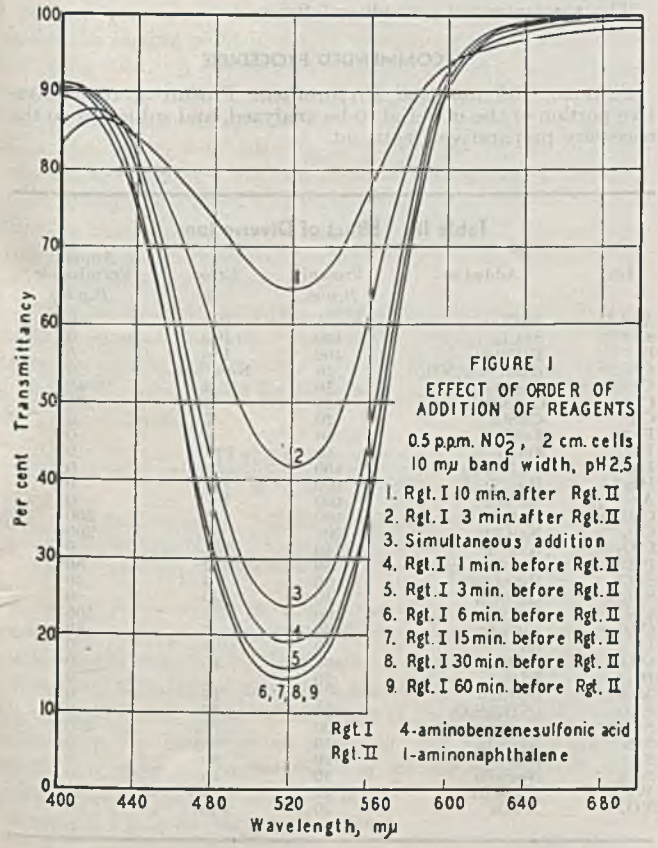
pH	Minutes Required: Diazotization	Coupling
1.12	1	60
1.38	..	30
1.64	..	20
2.00	3	10
2.15	..	7
2.29	..	5
2.58	6	3
3.00	6	2
3.38[a]	9	.
3.59[a]	12	.
3.67[a]	15	..

[a] Incomplete color development at these pH values.

EFFECT OF REAGENT CONCENTRATION. For 50 ml. of a solution containing 0.4 p.p.m. of nitrite, a minimum of 0.20 ml. of 4-aminobenzenesulfonic acid solution and 0.20 ml. of 1-aminonaphthalene solution is required. A tenfold excess of either reagent has no further effect upon the color developed. The acid required was added independently to maintain uniform acidity.

EFFECT OF ORDER OF ADDITION OF REAGENTS. The order of addition of reagents is of utmost importance. Figure 1 shows that the diazotization reaction with 4-aminobenzenesulfonic acid must be complete before 1-aminonaphthalene is added. Any unreacted nitrite still present when the coupling agent is added is partially destroyed by the amino group of the latter.

EFFECT OF pH. To establish the most desirable acidity, samples were buffered at different pH values by means of hydrochloric acid, hydrochloric acid–potassium chloride and acetic acid–sodium acetate combinations. The diazotization and coupling times required at room temperature for these various acidities are listed in Table I. These values were determined from curves similar to those in Figure 1. In Figure 1, 6 minutes' diazotization time is required at a pH of 2.5. It was further noted that full color is developed within 3 minutes after the addition of the coupling agent. High acidities increase the diazotization rate and decrease the coupling rate. Low acidities decrease



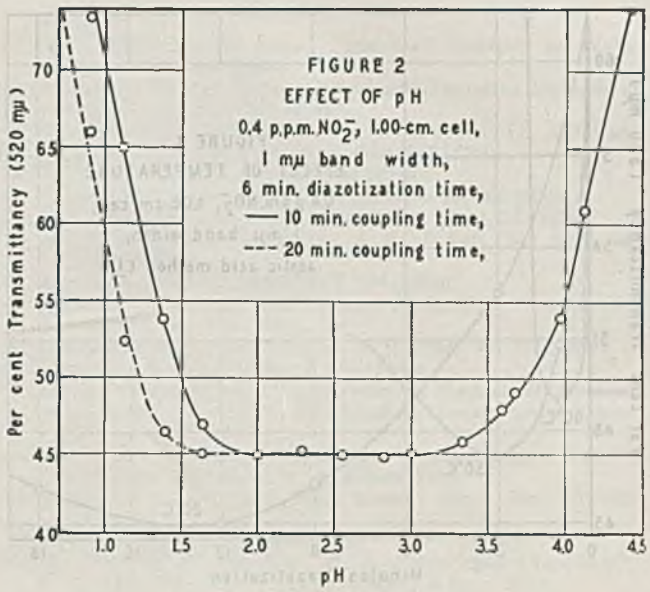


Table II. Effect of Temperature on Reaction Rates

Process	pH	Minutes Required: 20° C.	30° C.
Acetic Acid Method (*1*)			
Diazotization	3.1	12	9
Coupling	2.8	3	2
Hydrochloric Acid Method (*15*)			
Diazotization	2.1	9	6
Coupling	2.0	12	10
Hydrochloric Acid–Sodium Acetate			
Diazotization	1.4	2	1
Coupling	2.5	4	3

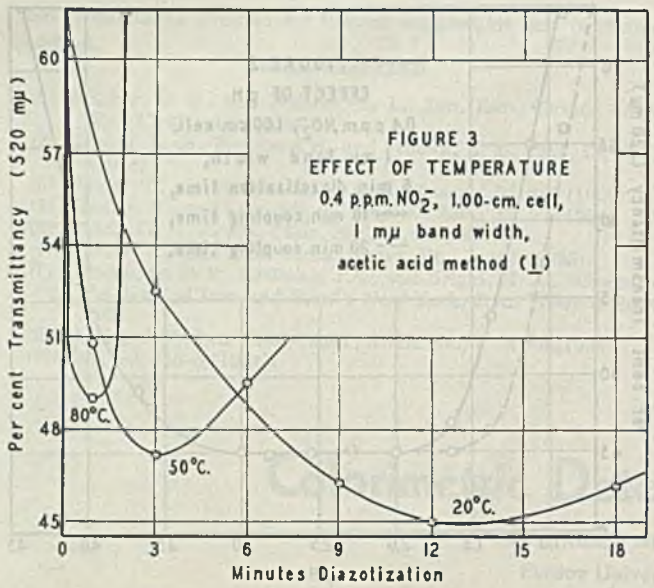
the diazotization rate and increase the coupling rate. This might have been predicted by the principle of mass action from Equations 1 and 2 in which the hydrogen ion is a reactant and a product, respectively.

The transmittancies at 520 mμ for these samples at various pH values are plotted in Figure 2, allowing 6 minutes' diazotization time and 10 minutes' coupling time, which were chosen as reasonable times. As indicated in Table I, incomplete color development in high acidities is due to incomplete coupling and in low acidities is due to incomplete diazotization. Increasing the coupling time brings about full color development in slightly more acidic samples, but increasing diazotization time does not bring about full color development in samples of lower acidity.

The colorimetric stability of the system is found to increase as the acidity increases.

After a study of Table I, it was decided to add 20 ml. of concentrated hydrochloric acid to the first reagent before diluting it to 100 ml. The resulting pH during diazotization is about 1.4. After adding the second reagent, the system is buffered with sodium acetate to a pH which will permit reasonably rapid coupling combined with a reasonable color stability. A pH of from 2.0 to 2.5 is considered best for general purposes. However, a slowly coupling, stable system can be had by buffering to a pH of 1.7 to 2.0, or a rapidly coupling, briefly stable system can be had by buffering to a pH of 2.5 to 3.0.

EFFECT OF TEMPERATURE. Figure 3 shows the effect of temperature on the diazotization reaction at a pH of 3.1. Since the reaction at this pH is slow, any effect of temperature can be readily measured. As the temperature increases, the rate of reaction increases as indicated in Table II and Figure 3. It is



evident, however, that the diazotization product is unstable both on heating and on long standing. In the highly acidic solution herein recommended, the reaction proceeds rapidly without heating, and the diazonium salt formed is relatively stable.

Effect of Light. This determination should be carried out in artificial light of moderate intensity. The reaction mixture should be shielded from direct sunlight, especially during diazotization, because, as Holbourn and Pattle (*7*) have found, diazotization products are photochemically unstable.

Effect of Nitrite Concentration. The lower limit of nitrite content which can be determined by this method is fixed by the maximum cell length available; the upper limit is fixed by the solubility of the colored dye. The exact concentration at which the dye precipitates is difficult to determine, as it varies under different conditions. Under the conditions here recommended, concentrations up to 0.6 p.p.m. of nitrite do not precipitate within 30 minutes. Beer's law holds up to a concentration of 0.6 p.p.m. for a 10 mμ band width. Reliable determinations can be made in the range of 0.025 to 0.600 p.p.m. of nitrite ion in a 2-cm. cell. As little as 0.0005 p.p.m. of nitrite nitrogen can be determined by the use of 24-cm. Nessler tubes.

Effect of Diverse Ions. In general, the effect of 400 p.p.m. of diverse ions on the analysis of a solution containing 0.4 p.p.m. of nitrite was determined. The quantities of interfering diverse ions which may be present without causing an error greater than 2% in the nitrite content are shown in Table III.

Of the diverse ions studied, the following did not interfere when present in concentrations 1000 times that of the nitrite: barium, beryllium, calcium, lead (II), lithium, magnesium, manganese (II), nickel (II), potassium, sodium, strontium, thorium, uranyl, zinc, arsenate, benzoate, borate, bromide, chloride, citrate, fluoride, formate, iodate, lactate, molybdate, nitrate, oxalate, phosphate, pyrophosphate, salicylate, selenate, sulfate, tartrate, tetraborate, and thiocyanate.

The interfering ions fall into various classes. Amines, oxidizing agents, and reducing agents destroy nitrites. Some ions complex the nitrite and retard its activity. Some ions precipitate under reaction conditions; others upset the acidity conditions; and still others interfere because of their own color.

Amines such as ammonia, urea, and aliphatic primary amines (HNH_2, NH_2CONH_2, and RNH_2) react with nitrites to liberate gaseous nitrogen. Small concentrations of ammonium ion did not interfere in this study but high concentrations should be avoided.

Nitrites are destroyed by reducing ions such as iodide, iron (II), chlorostannite, sulfide, thiosulfate, and sulfite, which must be absent from the sample. Strong oxidizing ions such as permanganate, chlorate, trisulfatocerate, perchlorate, periodate, peroxydisulfate, and tungstate should be absent. Other oxidizing ions such as dichromate, iodate, and selenate did not show any destruction of nitrite in these extreme dilutions in the time allowed in this study, but they may on longer standing.

Mercury (I) and silver precipitate as their chlorides, and bismuth and antimony (III) presumably as their oxychlorides in the presence of the hydrochloric acid used. Lead (II) also precipitates as its chloride in concentrated solution but redissolves at room temperature upon dilution to 400 p.p.m. and causes no interference. Chloroplatinate, iron (III), gold (III), and metavanadate ions form precipitates with 1-aminonaphthalene.

Alkali salts of ions such as carbonate, acetate, cyanide, and silicate reduce the acidity of the system and should be present only in limited quantities. The chlorostannate solution used contained hydrochloric acid. Its high acidity limited the amount to 40 p.p.m.

Mercury (II) causes high results, whereas copper (II) catalyzes the decomposition of the diazonium salt, causing low results. Both should be absent.

Purple ions, such as cobalt (II), which absorb green light, should be limited in concentration; whereas green ions, such as nickel (II) have little effect. Pale yellow ions, such as uranyl, show little interference; whereas more intensely yellow dichromate should be limited to 80 p.p.m. Chromium (III) should be limited to 40 p.p.m. All these colored ions change the hue of the system and must be absent for visual comparison.

DISCUSSION

In the present investigation, four requirements of a satisfactory method were found:

1. Diazotization should be carried out in strongly acidic solution.
2. Diazotization should be carried out in as cool a solution as is practicable.
3. Coupling should not be attempted until diazotization is complete.
4. Coupling should be carried out in as low an acidity as is consistent with colorimetric stability.

The acetic acid procedures (*1*, *8*) do not meet the first requirement; the elevated temperature procedures (*8*, *12*, *16*) do not meet the second; the mixed reagent procedures (*11*, *12*, *16*) do not meet the third; and the hydrochloric acid procedures (*13*) do not meet the fourth requirement.

The recommended procedure follows:

RECOMMENDED PROCEDURE

Sample. *Selection and Preparation.* Procure a representative portion of the material to be analyzed, and subject it to the necessary preparative treatment.

Table III. Effect of Diverse Ions

Ion	Added as:	Present P.p.m.	Error %	Amount Permissible P.p.m.
Au^{+++}	$AuCl_3$	5	Ppt.	0
Sb^{+++}	$SbCl_3$	400	Ppt.	0
Bi^{+++}	$Bi(NO_3)_3$	400	Ppt.	0
Ce^{++++}	$(NH_4)_2Ce(NO_3)_6$	20	New hue	0
Cr^{+++}	$Cr_2(SO_4)_3$	80	3	40
Co^{++}	$Co(NO_3)_2$	400	8	100
Cu^{++}	$CuSO_4$	20	7	0
Fe^{++}	$FeSO_4$	40	4	0
Fe^{+++}	$FeCl_3$	10	Ppt.	0
Hg^{++}	$Hg(NO_3)_2$	400	50	0
Hg_2^{++}	$Hg_2(NO_3)_2$	400	Ppt.	0
Ag^+	$AgNO_3$	400	Ppt.	0
$C_2H_3O_2^-$	$NaC_2H_3O_2$	400	3	200
CO_3^{--}	Na_2CO_3	200	2	200
ClO_3^-	$KClO_3$	40	4	0
$PtCl_6^{--}$	H_2PtCl_6	80	2	80
$SnCl_6^{--}$	H_2SnCl_6	80	3	40
$SnCl_4^{--}$	H_2SnCl_4	40	90	0
CN^-	KCN	200	4	100
$Cr_2O_7^{--}$	$K_2Cr_2O_7$	80	2	80
I^-	KI	10	3	0
ClO_4^-	$KClO_4$	400	15	0
IO_4^-	KIO_4	20	3	0
MnO_4^-	$KMnO_4$	1	14	0
$S_2O_8^{--}$	$(NH_4)_2S_2O_8$	400	37	0
SiO_3^{--}	Na_2SiO_3	400	5	200
SO_3^{--}	Na_2SO_3	40	88	0
S^{--}	Na_2S	10	80	0
$S_2O_3^{--}$	$Na_2S_2O_3$	40	23	0
WO_4^{--}	Na_2WO_4	40	3	10
VO_3^-	KVO_3	20	Ppt.	0

Measurement. Weigh or measure by volume a quantity of sample containing 0.03 mg. or less of nitrite.

Treatment. Most samples in water analysis need no further treatment. The proper treatment of other materials depends on the nature of the sample. Basic or acidic samples are neutralized with hydrochloric acid or sodium hydroxide.

DESIRED CONSTITUENT. *Separation.* If interfering ions are present, they should be complexed or removed to within the permissible concentrations given in Table III.

Measurement. To the sample in a 50-ml. volumetric flask add 1.0 ml. of acidified 4-aminobenzenesulfonic acid reagent. (To prepare this reagent, completely dissolve 0.60 gram of 4-aminobenzenesulfonic acid in about 70 ml. of hot water, cool the solution, add 20 ml. of concentrated hydrochloric acid, dilute to 100 ml. with water, and mix thoroughly.) Mix well. Allow at least 3, and not more than 10, minutes for diazotization at room temperature in diffuse light. Then add 1.0 ml. of 1-aminonaphthalene hydrochloride reagent (0.60 gram of 1-aminonaphthalene hydrochloride and 1.0 ml. of concentrated hydrochloric acid diluted to 100 ml. with water) and buffer the system to a pH of 2.0 to 2.5 with sodium acetate. This requires about 1.0 ml. of filtered 2.0 *M* sodium acetate solution. Dilute to volume and mix well. After 10 minutes, measure the intensity of the reddish purple color by the usual means. All measurements should be made within 30 minutes. Spectrophotometric measurements can be made at 520 mμ. A green filter, such as a Corning No. 401 of suitable thickness, is recommended for filter photometers. Permanent standards for visual comparisons have been suggested (*4*).

For minute amounts of nitrite, add the reagents according to the above procedure to 50 ml. of sample in a Nessler tube. The color developed is compared with a series of temporary or permanent standards.

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ABSTRACTED from a thesis presented by B. F. Rider to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of master of science, October, 1944.

Rapid Estimation of Effect of Pressure upon Boiling Points of Organic Compounds

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IT IS frequently convenient in laboratory distillations under reduced pressure to have at hand a means for estimating rapidly the boiling point of a substance at pressures other than that being used. A special case is finding the approximate boiling point at atmospheric pressure by extrapolation from a single boiling point value obtained at some reduced pressure. Another useful application is in selecting in advance a suitable reduced pressure for distilling a compound whose boiling point at atmospheric pressure is known. In these cases, a high degree of accuracy is usually unnecessary, and the consideration of accuracy is offset by the convenience of having a generally applicable process of calculation or extrapolation.

Numerous methods have been proposed for estimating boiling points at reduced pressure or finding the vapor pressure of substances at various temperatures. One of the most useful is that of Cragoe (*1*) as modified by Hass and Newton (*4*), which employs the equation:

$$\Delta t = t' - t = \frac{(273.1 + t)\ (2.8808 - \log p)}{\phi + 0.15\ (2.8808 - \log p)} \qquad (1)$$

where t' = boiling point, ° C. at atmospheric pressure
t = boiling point, ° C. at pressure p (mm.)
ϕ = entropy of vaporization at 760 mm. divided by 2.3 R

Hass and Newton have modified Cragoe's classification of compounds into eight groups according to their physical or structural relationship, and have established values for ϕ for each group.

However, calculation using this equation is rather cumbersome and time-consuming. The object of the present paper is to reformulate the Hass-Newton equation, and to derive graphs suitable for rapid interconversion and for use especially in the ordinary laboratory type of distillation.

Equation 1 may be rearranged to give:

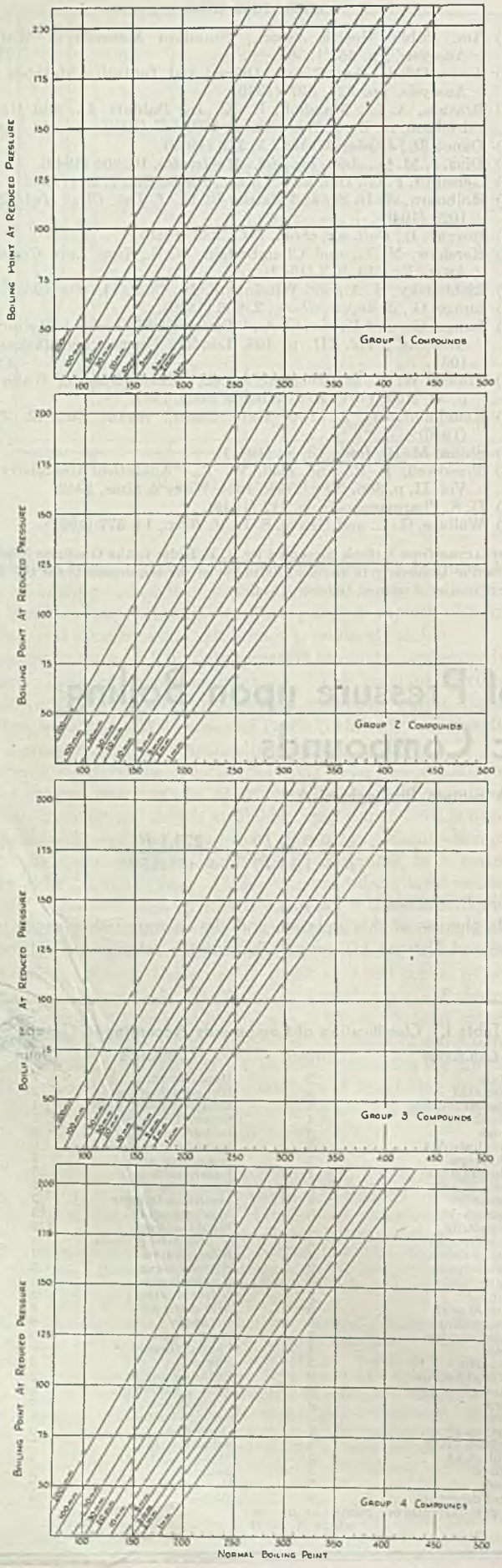
$$t = t' \frac{(\phi + 0.15\ P)}{(\phi + 1.15\ P)} - \frac{273.1\ P}{\phi + 1.15\ P} \qquad (2)$$

where $P = 2.8808 - \log p$.

By the use of this equation and the entropy values given by Hass and Newton (*3*), graphs showing the relationship between

Table I. Classification of Compounds According to Groups

Compound	Group	Compound	Group
Acetals	3	Heptylic acid	7
Acetic acid	4	Hydrocarbons, sat.	2
Acetic anhydride	6	Hydrocarbons, unsat.	1
Acetophenone	4	Isoamyl alcohol	7
Amines	3	Isobutyl alcohol	8
n-Amyl alcohol	8	Isobutyric acid	6
Anthracene	1	Isocaproic acid	7
Anthraquinone	1	Lauric acid	5
Benzaldehyde	2	Laurylamine	7
Benzene	2	Methyl salicylate	2
Benzoic acid	5	Myristic acid	5
Benzonitrile	2	Naphthalene	2
Benzophenone	2	α- and β-Naphthols	3
Benzoyl chloride	3	Nitroalkanes	3
Bromobenzene	2	Nitrobenzene	3
Butyric acid	7	Nitrotoluenes	2
Camphor	2	Nitrotoluidines	2
Caprylic acid	5	Allo-ocimene	1
Chloroanilines	3	Octanols	8
Chlorobenzene	2	Oleic acid	5
Cresols	4	Phenanthrene	1
Coumarin	2	Phenol	5
Dibenzyl ketone	2	Phthalic anhydride	2
Dimethyl oxalate	4	α- and β-Pinenes	1
Esters	3	Propionic acid	5
Ethers	2	*n*-Propyl alcohol	8
Ethylene glycol	7	Quinoline	2
Ethylene oxide	3	Sebacic acid	7
Formic acid	3	Stearic acid	5
Furfural	2	Sulfides	2
Glycols	7	Valeric acid	7
Glycol diacetate	4	Water	6
Halogen derivatives	Same group as where $X = H$		


Boiling Point At Reduced Pressure
Group 1 Compounds
Group 2 Compounds
Group 3 Compounds
Group 4 Compounds
Normal Boiling Point

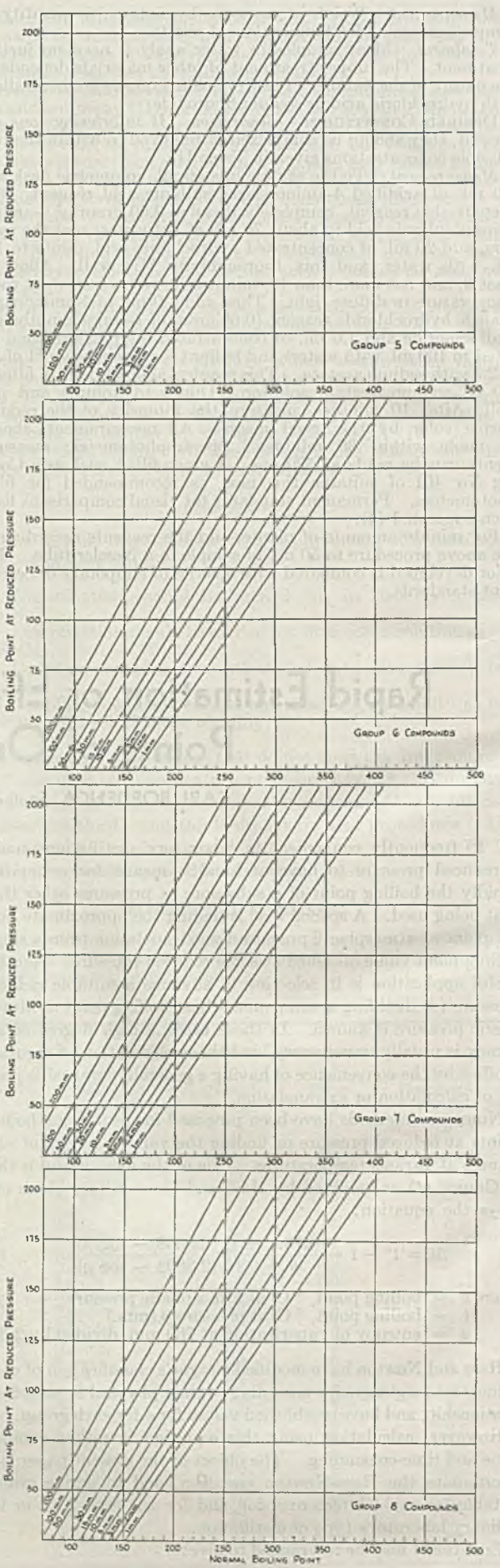

Boiling Point At Reduced Pressure
Group 5 Compounds
Group 6 Compounds
Group 7 Compounds
Group 8 Compounds
Normal Boiling Point

Table II. Comparison of Observed and Estimated Boiling Points

Compound (Group) Boiling point	Coumarin (2) Obs.	Coumarin (2) Est.	Acetophenone (4) Obs.	Acetophenone (4) Est.	Ethylene Glycol (7) Obs.	Ethylene Glycol (7) Est.
Pressure						
200 mm.	...	...	154	155	158	158
100 mm.	220	218	133	135	140	139
50 mm.	196	196	115	118	125	124
20 mm.	171	170	94	96	105	105
10 mm.	154	152	81	81	92	91
5 mm.	139	136	69	70	80	79

the normal boiling point and the boiling point at reduced pressure for the eight groups of compounds have been constructed. The classification of the compounds and families of compounds given in Table I is adapted from the reference articles (*3*, *4*). It is suggested that compounds not given in the table be classified in the group with compounds which they most closely resemble. In this connection, Cragoe (*1*) has pointed out that higher members of a series of compounds are usually in the same group, while the first members are generally in a different group. Boiling point values for intermediate pressures may be obtained from the charts by interpolation.

In general, the observed and estimated values have been found to agree satisfactorily. Representative results are shown in Table II, which gives a comparison of estimated and observed values for typical compounds of different groups. The observed values given for ethylene glycol have been obtained by interpolation of values reported by de Forcrand (*2*).

ACKNOWLEDGMENT

The author wishes to thank H. B. Hass and R. F. Newton for their valuable comments.

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Nephelometric Determination of Small Amounts of Sodium

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A rapid nephelometric method for determining small amounts of sodium salts in either liquids or solids is disclosed. An alcoholic uranyl magnesium acetate reagent is employed, and comparative data are given to indicate the sensitivity of various alcoholic compositions. The method is accurate to approximately 1 grain per gallon of sodium salts, expressed as sodium chloride in water analysis, and to ±0.003%, expressed as sodium oxide on solid samples. The method is particularly adaptable to routine analytical problems.

THE advantages of employing alcoholic magnesium uranyl acetate reagents, or of incorporating alcohol in some manner before the precipitation of the sodium uranyl acetate triple salt, have been disclosed by several workers (*1*, *2*, *3*). The need for a very rapid, sensitive method for determining traces of sodium salts in a solid product suggested the advisability of trying to employ an alcoholic reagent in the development of a nephelometric procedure. By modifying the method of Caley, Brown, and Price (*1*), a satisfactory procedure has been developed which is particularly useful for control analyses in the manufacture of solids with low sodium salt impurity specifications, but which may also be adapted to rapid estimation of sodium salt concentrations in liquids.

APPARATUS

The photometer used in this investigation employed a Nalco blue photofilter, a General Electric light-sensitive cell (Catalog No. 88 × 565), a General Electric Mazda lamp No. 51 (6 to 8 volts), and an ammeter (Model 26) manufactured by Simpson Electric Co., Chicago, Ill.

The specifications on the construction of the apparatus are:

Distance from light source to cell	50 mm.
Distance from light source to filter	25 mm.
Slit in screen	6.5 mm. wide × 16 mm. high
Length of path of light through solutions	16 mm.
Thickness of cell walls	2 mm.

REAGENT AND SOLUTIONS

ALCOHOLIC MAGNESIUM URANYL ACETATE. To 30 grams of uranyl acetate dihydrate, 150 grams of magnesium acetate tetrahydrate, and 20 ml. of glacial acetic acid are added 500 ml. of alcohol and sufficient water to make up to 1 liter. The resultant is heated on the steam bath, with stirring, until the salts are dissolved. Care must be taken to lose as little solvent as possible during the solution step. The reagent is then stirred until cool, and filtered without further dilution into a brown glass bottle.

Potassium chloride, lithium chloride, and sodium chloride solutions were prepared by dissolving the pure chemicals in triply distilled water.

PRELIMINARY EXPERIMENTS

Although, after an extensive investigation on the value of precipitating the triple salt in an alcoholic medium, Greene (*2*) came to the conclusion that the alcohol could not be incorporated into the reagent, the ease of controlling the precipitation medium when using only one reagent was especially appealing for the development of a nephelometric procedure where uniform crystal growth is imperative. In their earlier work, Caley, Brown, and Price (*1*) had successfuly employed an alcoholic reagent, and the authors' preliminary work was done using a slight modification of their reagent, but substituting the nephelometric procedure for their more complex and critical centrifugal estimation method. The study of reagents prepared using various alcohols was the initial step in the investigation of the method. In Figure 1 are plotted representative transmittancy curves for reagents made from methanol, ethanol, isopropanol, a mixture of ethanol and

Table I. Comparison of Sensitivity of Reagent Prepared from Methanol-Ethanol Mixtures

NaCl Added	Ethanol	9 Volumes Ethanol, 1 Volume Methanol	8 Volumes Ethanol, 2 Volumes Methanol	7 Volumes Ethanol, 3 Volumes Methanol	6 Volumes Ethanol, 4 Volumes Methanol	Methanol
Grains/gal.	*Per cent transmittancy*					
0	91.9	91.0	91.5	91.0	90.0	90.0
2	88.0	87.0	86.5	88.0	88.5	90.0
5	83.0	83.0	82.5	83.0	84.0	90.0
10	77.0	78.0	77.0	77.0	80.0	88.0
15	72.0	73.0	73.0	73.0	76.5	84.0
20	69.5	69.5	70.0	69.5	71.0	80.0
25	67.0	67.5	67.5	67.0	69.5	75.0

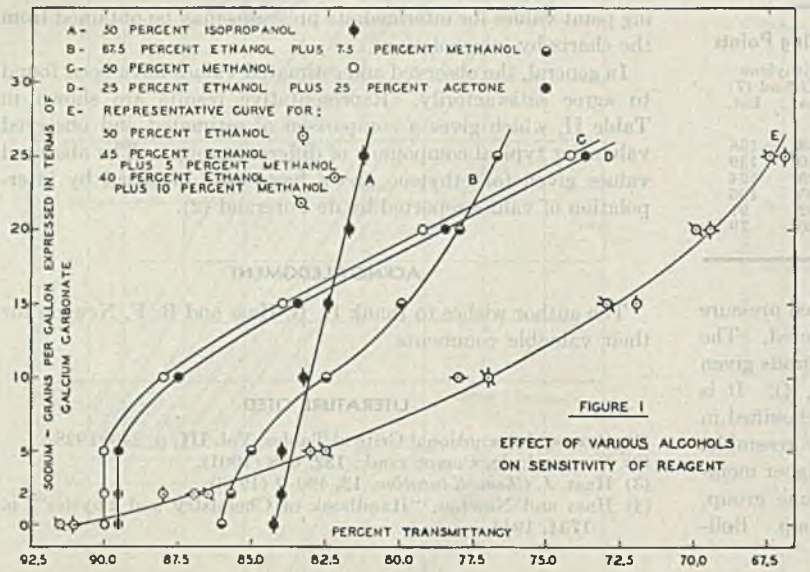

FIGURE I
EFFECT OF VARIOUS ALCOHOLS ON SENSITIVITY OF REAGENT

PROCEDURE

To 2 ml. of the solution to be tested in the test cell are added one drop of C.P. concentrated hydrochloric acid and 15 ml. of the alcoholic reagent. The two solutions are mixed by inverting five times, allowed to stand 5 minutes, and again mixed by inverting five times. After an additional 5-minute period of standing, the transmittancy is read and the sodium content determined by interpolation from a previously prepared standard transmittancy curve.

RESULTS

SOLUTIONS. In Table III are tabulated the results obtained by adding known amounts of sodium ion as sodium chloride to natural raw waters. The accuracy of this rapid procedure is approximately 0.000015 gram per cc. (1 grain per gallon) expressed in terms of sodium chloride.

Relatively high concentrations of lithium and potassium ions do not affect the accuracy of the sodium determination. The results obtained, using a standard 10 grains per gallon sodium chloride water to which was added varying amounts of lithium and potassium salts, are shown in Table IV.

SOLIDS. The procedure was developed primarily for analytical control in the manufacture of fluid cracking catalyst for the petroleum industry. It was found that nearly 100% of the sodium salts could be extracted from this siliceous material by boiling for 2 minutes in 1 to 1 hydrochloric acid.

To 10 grams of catalyst are added 20 ml. of 1 to 1 hydrochloric acid, and the mixture is boiled exactly 2 minutes. After filtering, 10 ml. of alcoholic reagent are added to 2 ml. of filtrate, the two solutions mixed by inverting 5 times, allowed to stand 5 minutes, and mixed again by inverting 5 times, and the transmittancy is determined after an additional 5 minutes. In Table V, the results of this rapid method are compared with results obtained by the standard gravimetric procedure. The accuracy of the method can be considered to be 0.003% expressed as Na_2O.

Table II. Stability and Reproducibility of Reagent

NaCl Added	Reagent Batch 1	Reagent Batch 2	Reagent Batch 3
Grains/gal.	*Per cent transmittancy*		
0	91.0	91.5	90.5
2	87.0	87.0	86.5
5	83.5	83.0	83.0
10	79.0	78.0	78.0
15	73.0	74.0	73.0
20	69.5	69.5	69.5
25	67.5	68.0	68.0
35	63.0	63.0	63.0

Table III. Analysis of Solutions

	Water A	Water B
Total hardness as $CaCO_3$, grains per gallon	8.7	37.0
Calcium as $CaCO_3$, grains per gallon	5.2	30.0
Sodium as NaCl, grains per gallon	1.5	7.9
Silica, p.p.m. SiO_2	9.7	10.7

NaCl Added	NaCl Found	NaCl Added	NaCl Found
Grains per gallon			
0.0	1.5	0.0	7.9
5.0	6.5	5.0	12.9
10.0	11.5	10.0	17.9
17.5	19.0	17.5	23.5

Table IV. Interference of Potassium and Lithium

NaCl Present *Grains/gal.*	Salt Added *Grains/gal.*	% Transmittancy
10	None	88.0
10	LiCl 2.5	88.0
10	LiCl 5.0	88.0
10	LiCl 10.0	87.5
10	LiCl 20.0	88.0
10	KCl 2.5	87.5
10	KCl 5.0	88.0
10	KCl 10.0	88.0
10	KCl 20.0	88.0

Table V. Analysis of Solid Materials

Sample	Na_2O Gravimetric %	Na_2O Found %
1	0.0195	0.017
2	0.010	0.008
3	0.019	0.021
4	0.012	0.009

acetone, and a representative curve for methanol-ethanol mixtures.

From these data, it is apparent that ethanol reagents, or ethanol reagents containing small quantities of methanol, are more sensitive than methanol or isopropanol reagents. Incorporating acetone, or increasing the alcohol content above 50% by volume, rendered the reagent less sensitive. The disadvantage of an increase in the alcohol content of the precipitation medium was apparently due to the enhanced crystal growth, which caused the precipitated sodium salt to settle very rapidly, thereby decreasing the accuracy of the transmittancy measurement. The possibility of using ethanol denatured with methanol was of special interest because of the relative ease of obtaining such mixtures. Table I shows the effect of increased methanol-ethanol ratios. Volume ratios of 3 to 7 can be tolerated before the detrimental influence of methanol is appreciable. Therefore, because of the availability of Formula 30 alcohol (10% methanol and 86% ethanol by volume), it was selected for the preparation of the reagent. Table II gives data illustrating the stability and reproducibility of this alcoholic reagent. Reagents 1, 2, and 3 were prepared about 5 days apart. The results are well within the limits of accuracy of the method.

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Colorimetric Determination of Phenols

Application to Petroleum and Allied Products

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A colorimetric method is described for determination of the total phenolic content of hydrocarbon mixtures, organic solvents, aqueous solutions, and concentrated phenols. The method is not affected by organic materials containing other functional groups (such as aldehydes or ethers) nor by water, mineral acids, inorganic bases, or inorganic salts. In this procedure the sample, or a caustic extract thereof, is dissolved in acetic acid, nitrous acid solution is added to form the respective nitrosophenol, and after a short reaction period an excess of alcoholic ammonium hydroxide is added. After standing, the intensity of the resulting colored quinoid salt is measured with a photoelectric colorimeter and related to that of a calibration curve which has been prepared under identical conditions by concentrations of a standard phenol sample. Although the method was primarily developed for the determination of monohydroxy alkyl phenols in refined petroleum products, it has been successfully applied to the determination of monohydroxy- and dihydroxyphenols in a variety of materials such as crude oil, oil additives, solvents, polymers, plastics, cresylic acids, and caustic treating solutions.

DURING the past decade a need has developed for the determination of phenols, particularly monohydroxyphenols, in a variety of materials. This need has become increasingly important to the petroleum chemist because the presence of phenols often affects the behavior of many petroleum products. For example, the presence of small amounts of phenols in paint and varnish thinners has been known to retard the drying rate of these products, and phenolic compounds have found use in gasoline as antioxidants to prevent gum formation, light instability, etc. Experience has shown that there is need of a general method because the phenolic compounds encountered are usually a mixture of various unknown phenols and because it is necessary to apply the method in the presence of materials such as alcohols, acids, amines, ethers, aldehydes, ketones, water, organic sulfur derivatives, and inorganic compounds. Such characteristics as rapidity and accuracy are secondary in importance to precision and universal applicability.

A review of the literature reveals a number of qualitative tests for phenols, most of which have been studied and classified by Gibbs (*2*). Only a few of the qualitative tests are adaptable to the quantitative determination of phenols because many of the reactions are applicable only to certain types of phenols and because many are not specific for phenols, reacting similarly with other types of compounds.

Included among these methods of limited application are those of Houghton and Pelly (*4*), which involves oxidation of the phenol to an indophenol by hypochlorite in the presence of *p*-aminodimethylaniline, of Gibbs (*3*), in which the phenol is reacted with quinone chloroimide to form a colored indophenol, and of Folin and Denis (*1*), wherein phenolic compounds of phosphomolybdicphosphotungstic acid are reduced to the lower oxides of molybdenum and tungsten, resulting in the formation of blue solutions.

Stoughton (*5*) devised a method which depends upon treatment of the phenol with nitric and sulfuric acids at approximately 100° C. to form a nitrosophenol which rearranges in the presence of excess alcoholic ammonium hydroxide to form the highly colored quinoid radical. The probable reactions are:

$$2HONO_2 \xrightarrow{\text{organic matter}} 2HONO + O_2$$

$$RC_6H_4OH + HONO \xrightarrow{H_2SO_4} RC_6H_3\begin{matrix}OH\\NO\end{matrix} + H_2O$$

$$RC_6H_3\begin{matrix}OH\\NO\end{matrix} \xrightarrow{NH_4OH} \left[RC_6H_3\begin{matrix}O\\NO\end{matrix}\right]^- + H^+$$

The resulting colored solutions are compared with those from standard phenols by means of a visual colorimeter. This method is generally applicable to ortho, meta, and para substituted phenols. The colors produced by the reaction with different phenols range from greenish yellow to orange yellow. Wetlaufer, Van Natta, and Quattlebaum (*6*) used a modified version of the Stoughton procedure, applying it to the determination of traces of phenols in hydrocarbon solvents. They achieved high sensitivity by extracting the phenols with a small portion of dilute caustic solution.

The method presented here is a further modification of Stoughton's (*5*) nitrosophenol procedure. The significant differences are the use of sodium nitrite solution in place of nitric acid as the source of nitrous acid, formation of the nitrosophenol at room temperature under carefully predetermined conditions, and measurement of the colored solutions in a photoelectric colorimeter. As in the method of Wetlaufer *et al.* (*6*), the phenols are extracted from hydrocarbons prior to the color development. This procedure achieves greater sensitivity and avoids interference of large quantities of hydrocarbons. As a result of these changes, the proposed method is versatile, accurate, and applicable to a wide variety of materials.

APPARATUS

A sensitive photoelectric colorimeter equipped with light-absorption cells permitting passage of light through a depth of approximately 1 cm. of solution and equipped with a monochromatic light source consisting of either a lamp with color filters or a monochromator capable of producing light of narrow spectral range (50 mμ) which is predominantly violet (420 mμ).

REAGENTS

Potassium Hydroxide Solution, 10% aqueous.

Acetic Acid, C.P., glacial.

Buffer Solution. To prepare 1 liter of solution, mix 800 ml. of glacial acetic acid, 150 ml. of 10% potassium hydroxide solution, and 50 ml. of water.

Saturated Sodium Nitrite Solution, aqueous.

Alcoholic Ammonium Hydroxide Solution. To prepare 1 liter of solution, mix 450 ml. of anhydrous ethyl alcohol or isopropyl alcohol, 300 ml. of 14 *N* ammonium hydroxide, and 250 ml. of water.

Standard Phenol Solution, containing 0.1 mg. of the phenol to be determined per milliliter. Weigh accurately 0.1 ± 0.01 gram of the phenol in a 100-ml. volumetric flask and dilute to exactly 100 ml. with the buffer solution. Mix thoroughly, transfer a 10-ml. aliquot to a second 100-ml. volumetric flask, and dilute to the mark with the acetic acid buffer solution. Where maximum accuracy is essential be sure that the phenol used as a standard is the same as that determined. Where high accuracy is not essential, an arbitrary standard such as *p*-cresol may be used for the preparation of a calibration curve.

Sulfuric Acid, 36 *N*.

Diluent. Extract 1 liter of technical octane with 100 ml. of 10% potassium hydroxide solution and remove the aqueous layer. Extract a second time with the fresh caustic solution, then wash with 100 ml. of water and filter the hydrocarbon layer through a dry folded paper. When the sample is not soluble in octane, use other solvents such as benzene, toluene, ether, etc., purified in the same manner.

Table I. Relative Color Intensities Produced by Pure Phenols and Concentrated Phenol Mixtures

Material	Intensity[a] of Color Produced by 1 Mg. of Material Relative to Color from 1 Mg. of Petroleum Cresylic Acid (b.r. 220–225° C.)[b]
Petroleum cresylic acids	
Boiling range 220–225° C.[b]	1.00
Boiling range 200–220° C.[b]	1.42
Boiling range 200–225° C.[b]	1.34
Boiling range 200–235° C.[b]	1.06
Boiling range 220–240° C.[b]	0.81
Boiling range 225–245° C.[b]	0.79
Boiling range 235–290° C.[b]	0.56
Phenol	1.07
p-Cresol	1.24
o-Cresol	1.85
m-Cresol	0.73
p-Ethylphenol	1.21
o-Ethylphenol	1.82
m-Ethylphenol	0.76
2,4-Dimethylphenol	1.28
2,5-Dimethylphenol	0.68
2,6-Dimethylphenol	3.34
3,4-Dimethylphenol	0.93
3,5-Dimethylphenol	0.47
2,3,5-Trimethylphenol	0.52
2,4,6-Trimethylphenol	0.25
4-*tert*-Butyl-2,6-dimethylphenol	0.53
2,4-Dimethyl-6-*tert*-butylphenol	0.22[c]
p-*tert*-Amylphenol	0.95
α-Naphthol	2.26
β-Naphthol	0.83
Resorcinol	0.98
o-Chlorophenol	0.80
m-Aminophenol	0.5
Guaiacol	2.02
8-Hydroxyquinoline	1.50
Hydroquinone	0.55
Catechol	0.55
p-*tert*-Butylcatechol	0.19[c]
Carvacrol	1.33
p-Hydroxybenzoic Acid	0.03

[a] Spekker photoelectric absorptiometer, No. 7 (violet) filter.
[b] Nominal boiling range, initial to 95% point.
[c] Measurement by Klett-Summerson photoelectric colorimeter, No. 42 (violet) filter.

PROCEDURE

Two procedures are described below. The choice of the procedure to be used depends upon the type of material which is being analyzed for phenol content. The direct procedure is generally used for oxygenated materials, while the extraction procedure is used for hydrocarbons.

Direct Procedure. Use this procedure for materials soluble in the acetic acid buffer solution—i.e., cresylic acids, alcohols, naphthenic acids, glycerols, phenyl ethers, ketones, and aqueous solutions. In the case of highly colored or opaque materials giving rise to high blanks, use the extraction procedure.

Into a 100-ml. volumetric flask introduce an accurately weighed sample of the size indicated below:

Phenol Content, %	Sample Size, Grams
0.0 to 0.4	2
0.3 to 0.8	1
0.6 to 1.6	0.5
1.5 to 4	0.2
3 to 8	0.1

For phenol contents above 8% use approximately smaller samples or preferably 0.5- to 5-ml. aliquots of solution of sample in buffer solution; in all such cases regulate sample or aliquot to contain 3 to 8 mg. of phenol. Dilute the sample to exactly 100 ml. with the buffer solution, mix, and transfer a 5-ml. aliquot into a 50-ml. volumetric flask. By means of a medicine dropper, add 5 drops of 36 *N* sulfuric acid and 2 drops of saturated sodium nitrite solution. Mix by swirling, allow the mixture to stand 15 to 30 minutes (30 to 45 minutes if hydroxybenzene is the phenol present), and then slowly add alcoholic ammonium hydroxide solution while cooling the flask in ice water to make a total volume of exactly 50 ml. at room temperature. Allow the final solution to stand 1 hour or preferably overnight and obtain a colorimeter reading using a violet light source (420 mμ).

Make three blank determinations according to the above procedure. In the first omit the sodium nitrite solution but include a duplicate aliquot of the sample solution; in the second omit the sample but include the nitrite solution; and in the third omit both the sample and the nitrite solution. For the most accurate work determine all three blanks for each analysis. Otherwise, determine all blanks at least once whenever new reagents are used; determine the first blank only when the sample is colored.

Extraction Procedure. Use this procedure for materials which are insoluble in the acetic acid buffer solution but soluble in the diluent or similar solvents. Always remove phenol contaminants from solvent by the treatment outlined upon preparation of the diluent.

Introduce 10 ml. of 10% potassium hydroxide solution into a 125-ml. Squibb-type separatory funnel and add the volumes of sample and diluent as indicated in the following tabulation:

Phenol Content *Mg./100 ml.*	Volume of Sample *Ml.*	Volume of Diluent *Ml.*
0 to 100	50 ± 0.2	0
50 to 200	25 ± 0.1	25
100 to 500	10 ± 0.1	40
200 to 1000	5 ± 0.05	45

For phenol contents greater than 1000 mg. per 100 ml., weigh a proportionately smaller quantity of sample and add 45 to 50 ml. of diluent.

Stopper the separatory funnel and shake for 5 minutes. Allow the mixture to stand in the separatory funnel until two distinct layers have formed and carefully remove the lower layer without loss into a 100-ml. volumetric flask. Add a 5-ml. portion of potassium hydroxide solution to the separatory funnel, shake the mixture for 5 minutes, allow the phases to separate, and quantitatively withdraw the lower layer into the same volumetric flask. Add 5 ml. of distilled water to the separatory funnel, shake for 2 minutes, allow the phases to separate, and withdraw the aqueous layer into the volumetric flask containing the caustic extracts.

To the combined extracts, slowly add glacial acetic acid while cooling the flask in ice water to make a total volume of exactly 100 ml. at room temperature. Pipet a 1- to 5-ml. aliquot containing 0.05 to 0.5 mg. of phenol into a dry 50-ml. volumetric flask. If necessary, add sufficient of the acetic acid buffer solution to make a total volume of 5 ml. Proceed with the color development as outlined under the direct procedure (above), starting with "by means of a medicine dropper add 5 drops of 36 *N* sulfuric acid, etc."

PREPARATION OF CALIBRATION CURVES

Prepare a calibration curve showing the relation between the colorimeter readings and the phenol content as follows:

From a buret or pipet introduce 0, 1, 2, 3, 4, and 5 ml. of the standard phenol solution into separate dry 50-ml. volumetric flasks. Add sufficient acetic acid buffer solution to make a total volume of 5 ml. and proceed with the color development as outlined under the direct procedure (above), beginning with "by means of a medicine dropper add 5 drops of 36 *N* sulfuric acid, etc."

CALCULATIONS

Correct the colorimeter reading obtained for the sample by means of the following equation:

$$\text{Corrected reading} = R - (B_1 + B_2 - B_3)$$

where

R = colorimeter reading for the sample
B_1 = colorimeter reading obtained when sodium nitrite solution is omitted
B_2 = colorimeter reading when sample is omitted
B_3 = colorimeter reading when both sample and sodium nitrite solution are omitted

Note. Unless the samples or extracts are colored, B_2 will be the only significant correction and B_1 and B_3 will cancel each other. Besides making a color blank, the degree of color interference may sometimes be minimized by reducing sample or aliquot size.

Convert the corrected colorimeter reading to milligrams of phenol by means of the prepared calibration curve and express the results as percentage by weight of phenol or as milligrams of phenol per 100 ml. Report the phenol used as standard.

EXPERIMENTAL

Apparatus Used. A Spekker absorptiometer (photoelectric) was used for the color measurements during the early part of the investigation. Later a Klett-Summerson photoelectric colorimeter and Fisher electrophotometer were used for the investigational work as well as actual application of the method. A Coleman spectrophotometer (Model 10S) was used to obtain the spectral transmittance curves of the colored solutions.

Relative Color Intensities Produced by Various Phenols. Samples containing exactly 1 mg. of a number of pure phenols and commercial cresylic acids were treated by the proposed direct procedure, and the intensities of the colors produced were measured photoelectrically with a Spekker absorptiometer using the No. 7 (violet) filter supplied with the apparatus. The materials tested and the data obtained are given in Table I, expressing the intensity of color produced by 1 mg. of material relative to that from 1 mg. of petroleum cresylic acid (nominal boiling range 220° to 225° C., initial to 95% point) taken as unity. The order of magnitude of color intensity values obtained by use of other photoelectric colorimeters or visual colorimeters agrees with those in Table I, but there are small differences depending upon the spectral characteristics of the light filter used to make the tests or of the response of the eye by the visual method. This presents no difficulty, provided measurements for sample and standard are made with the same colorimeter. However, unless only rough approximation is adequate, the color values presented in Table I must be redetermined on the colorimeter at hand if it is desired to compute a given color measurement in terms of the various phenols.

From Table I it is seen that a wide variation exists in relative color intensities produced by the various phenolic compounds; this variation appears to be mainly influenced by the location of the substituted groups on the benzene ring. Of the monohydroxyphenols, the most intense colors are given by those phenols with alkyl groups in the ortho position with respect to the hydroxyl group; the least color is given by the most highly substituted compounds. Between these extremes no simple generalizations are valid. With concentrated phenol mixtures such as cresylic acids obtained from petroleum, the relative color intensity appears to decrease with an increase in average boiling point. With respect to pure phenols, the color intensity is not related linearly to the molecular weight. Of the thirty-six phenolic compounds or mixtures tested, only *p*-hydroxybenzoic acid failed to give a significant color by the proposed method. The cause of this anomaly is unknown at present.

Variation of Color Intensity with Concentration of Phenols. Calibration curves for use with photoelectric colorimeters were prepared for several pure phenols and phenol mixtures by treating various known weights of these compounds according to the proposed procedure. In Figure 1 are presented calibration curves for phenol, *p*-cresol, 2,6-dimethylphenol, 2,4,6-trimethylphenol, and petroleum cresylic acids (boiling range 220–225° C.) obtained with the Spekker absorptiometer using the No. 7 filter (violet) supplied with apparatus. In Figure 2 are presented the calibration curves for phenol, *o*-cresol, *m*-cresol, *p*-cresol, 3,5-dimethylphenol, 2,4-dimethyl-6-*tert*-butyl phenol, *p-ter*-butyl catechol, and petroleum cresylic acids (boiling range 220–225° C.), obtained with the Klett-Summerson photoelectric colorimeter using the No. 42 filter (violet) supplied with the apparatus.

With less than 1 mg. of phenol in the final solution substantially straight-line curves were obtained in most cases, indicating that Beer's law applies in this determination. This is particularly true of the calibration curves obtained for the Klett-Summerson colorimeter, which utilizes a light filter transmitting only a narrow band of light in the violet region (approximately 420 mμ). The Spekker light filter transmits some light in regions other than violet.

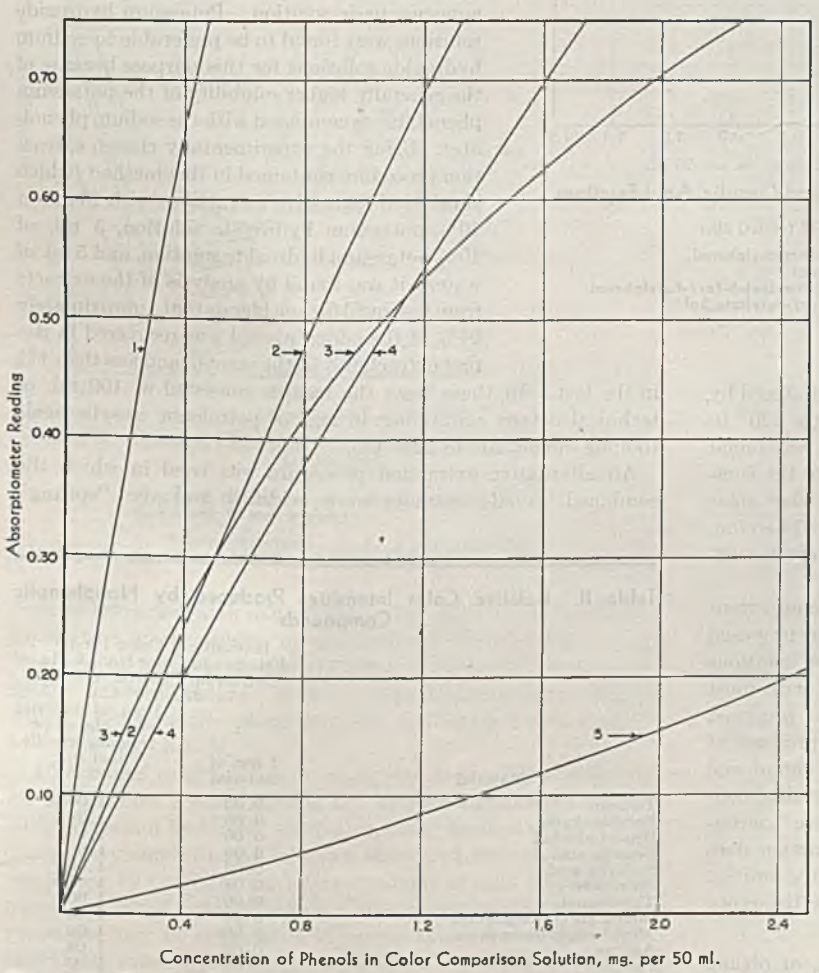

Figure 1. Typical Calibration Curves for Pure Phenols and Phenolic Mixtures

Spekker photoelectric absorptiometer, No. 7 (violet) filter

1. 2,6-Dimethylphenol
2. *p*-Cresol
3. Phenol
4. Petroleum cresylic acid (b.r. 220–225° C.)
5. 2,4,6-Trimethylphenol

Spectral Characteristics of Color Comparison Solutions. When treated by the proposed procedure, various monohydroxyphenols produce color comparison solutions which vary from greenish yellow for phenol and meta-substituted phenols to orange-yellow for other phenols. Dihydroxyphenols and naphthols generally produce brownish-yellow solutions. The various color shades are sufficiently distinct so that an experienced chemist can qualitatively divide them into three groups by visual examination. Figures 3, 4, and 5 give typical spectral transmittance curves for the color comparison solutions produced by a variety of pure phenols and cresylic acid fractions. In most cases the maximum light absorption occurs at wave lengths of 400 to 425 millimicrons. Because of this fact and because the light absorption bands are wide, the color intensity of the comparison solution can be measured by any type of photoelectric colorimeter, provided proper attention is given to the choice of light filter.

Interference by Nonphenolic Compounds. A number of nonphenolic compounds have been tested to determine whether or not they interfere with the phenol determination by exhibiting colors after treatment by the proposed procedure. The data presented in Table II were obtained with exactly 1-mg. samples of various nonphenolic compounds, both with and without blending with 1 mg. of petroleum cresylic acid (boiling range 220° to 225° C.). The values given for relative color intensities are

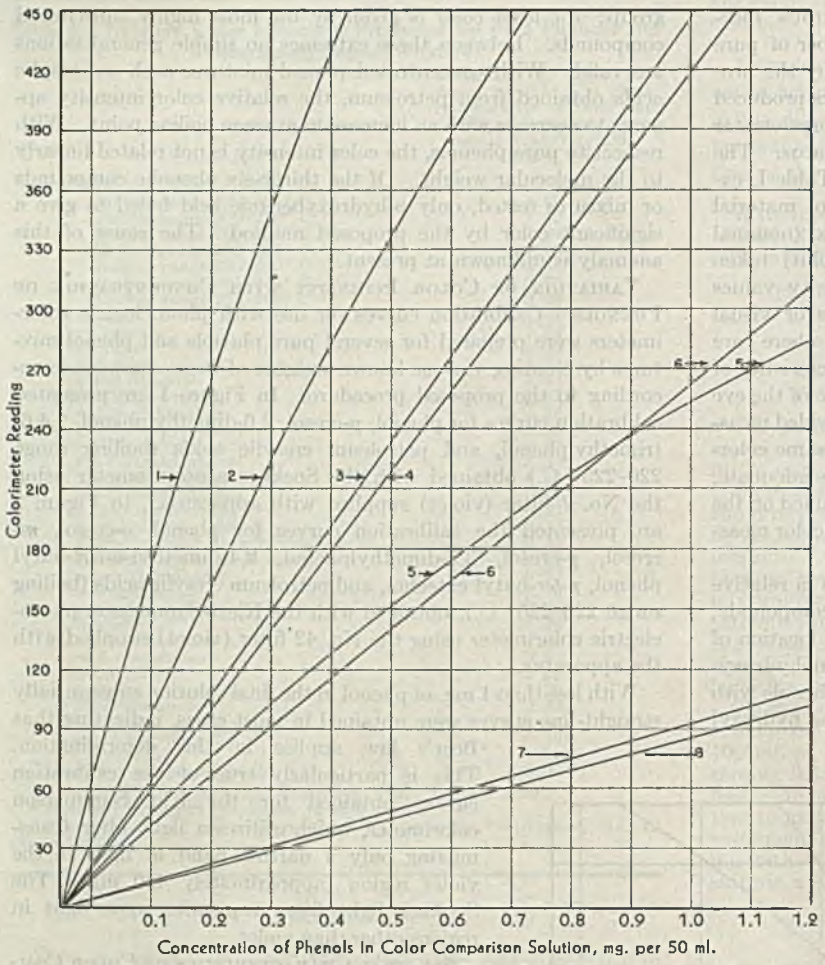

Figure 2. Typical Calibration Curves for Pure Phenols and Cresylic Acid Fractions

Klett-Summerson photoelectric colorimeter, No. 42 (violet) filter

1. o-Cresol
2. m-Cresol
3. Petroleum cresylic acid (b.r. 220–225° C.)
4. p-Cresol
5. 3,5-Dimethylphenol
6. Phenol
7. 2,4-Dimethyl-6-*tert*-butylphenol
8. p-*tert*-Butylcatechol

based on the value of unity for the intensity of color produced by exactly 1 mg. of petroleum cresylic acid (boiling range 220° to 225° C.). From these and numerous other tests it was found that with the exception of aniline and xylidine none of the common aliphatic or aromatic nonphenolic compounds give color comparison solutions of the type given by phenols. Therefore it can be assumed that the proposed method is with very few exceptions specific for phenolic materials.

Aniline and xylidine were found to interfere to some extent with the phenol determination; when treated by the proposed direct procedure, they reacted giving color comparison solutions having shade and intensity similar to those obtained with most phenols. However, experiments have shown that the proposed extraction procedure gives satisfactory results in the presence of these aromatic amines, provided the concentration of the phenol is at least twenty times greater than the aniline or xylidine concentration. For samples containing a higher relative concentration of aniline or xylidine, the usual caustic extraction does not generally result in an extract substantially free of the amines. In such cases the following modified procedure gives satisfactory results.

Weigh a sample containing approximately 15 mg. of phenol into a 125-ml. Squibb-type separatory funnel containing 100 ml. of phenol-free technical octane. Add 10 ml. of 5% sulfuric acid and shake the mixture vigorously for 5 minutes. Allow the phases to separate completely and withdraw the lower layer. Add 10 ml. of water to the separatory funnel, shake the mixture for 1 minute, and allow the two phases to separate. Withdraw the lower phase and add it to the lower phase from the first extraction. Repeat the acid and water extractions. Transfer back to the separatory funnel any hydrocarbon phase liberated from the combined acid and water extracts. Analyze the residual extracted hydrocarbon in the separatory funnel by the proposed extraction procedure.

Analyses of samples of some hydrocarbon mixtures, especially cracked gasolines to which known quantities of alkyl phenols had been added, frequently gave low results by the extraction procedure. Subsequent tests showed that the apparent phenol content of such samples tended to decrease with time. Analyses of these samples showed an appreciable concentration of peroxides; the peroxide content was found to increase with time. Apparently the added phenols were oxidized by compounds of the peroxide type resulting from air oxidation of the unsaturated hydrocarbons present. This behavior emphasizes the necessity of analyzing such materials immediately in order to prevent possible changes in phenol content on standing.

Extraction Procedure. The determination by this method of small amounts of phenols present in a hydrocarbon material requires concentration of the phenols by extraction from the hydrocarbon with a minimum quantity of an aqueous, basic solution. Potassium hydroxide solutions were found to be preferable to sodium hydroxide solutions for this purpose because of the generally higher solubility of the potassium phenolates as compared with the sodium phenolates. Using the experimentally chosen extraction procedure contained in this method (which consists of successive extractions with 10 ml. of 10% potassium hydroxide solution, 5 ml. of 10% potassium hydroxide solution, and 5 ml. of water), it was found by analysis of the extracts from technical octane blends that approximately 94% of the added phenol was recovered in the first extract, 6% in the second, and less than 1% in the last. In these tests the sample consisted of 100 ml. of technical octane containing 46 mg. of petroleum cresylic acids (boiling range 220° to 225° C.).

An alternative extraction procedure was tried in which the combined caustic extracts were acidified and the "sprung"

Table II. Relative Color Intensities Produced by Nonphenolic Compounds

Material	Intensity of Color Produced Relative to Color from 1 Mg. of Petroleum Cresylic Acid (b.r. 220–225° C.) 1 mg. of material	1 mg. of material + 1 mg. of petroleum cresylic acid (b.r. 220–225° C.)
Toluene	0.00	1.00
Benzaldehyde	0.00	1.00
Benzyl alcohol	0.00	1.00
Benzoic acid	0.00	1.00
Salicylic acid	0.02	1.00
Phenetole	0.08	1.00
Thiophenol	0.00	1.00
Mixed alkyl thiophenols	0.04	1.00
Mixed naphthenic acids	0.00	1.00
Aniline	0.05	1.08
Pyridine	0.00	1.00
Quinoline	0.00	1.00
Mixed nitrogen bases from petroleum	0.00	1.00
Mixed nonbasic nitrogen compounds from petroleum	0.00	1.00
Methyl ethyl ketone	0.00	1.00

Table III. Influence of Water Content of Reaction Medium on Intensity of Color Produced by Various Phenols

Phenol Present (1 Mg.)	Relative Color Intensity Using 5 Ml. of Acetic Acid Solution of Indicated Water Content					
	0[a]	5% volume	10% volume	20% volume	40% volume	60% volume
Phenol	1.00	1.05	1.00	1.00	0.30	0.20
p-Cresol	1.00	0.77	0.71	0.71	0.71	0.69
o-Cresol	1.00	1.11	1.18	1.29	0.95	0.69
m-Cresol	1.00	1.11	1.14	1.11	0.77	0.44
p-Ethylphenol	1.00	0.80	0.77	0.74	0.74	0.71
m-Ethylphenol	1.00	1.11	1.14	1.14	0.95	0.80
2,4-Dimethylphenol	1.00	1.43	1.54	1.67	1.67	1.67
2,5-Dimethylphenol	1.00	1.33	1.54	1.54	1.11	0.77
2,6-Dimethylphenol	1.00	2.50	3.60	4.40	4.40	4.00
3,4-Dimethylphenol	1.00	1.05	1.08	1.05	0.83	0.77
3,5-Dimethylphenol	1.00	1.15	1.20	1.07	0.86	0.64
2,3,5-Trimethylphenol	1.00	1.20	1.20	1.11	0.97	0.88
Petroleum cresylic acids						
Boiling range 200–220° C.	1.00	1.25	1.33	1.54	1.54	1.43
220–225° C.	1.00	1.33	1.33	1.33	1.43	1.43
220–240° C.	1.00	1.14	1.25	1.33	1.33	1.25
235–290° C.	1.00	1.15	1.25	1.30	1.20	1.15
200–235° C.	1.00	1.18	1.38	1.54	1.54	--

[a] Used as standard of comparison for each phenol only; not intercomparable.

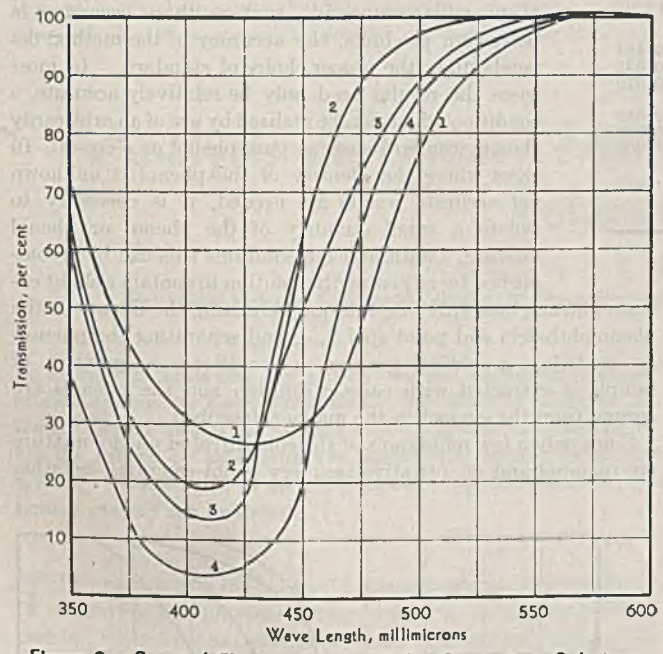

Figure 3. Spectral Characteristics of Color Comparison Solutions for Phenols

Instrument, Coleman spectrophotometer, Model 10S
Cell depth, 13 mm. (square)

1. 0.5 mg. of *p*-cresol
2. 0.5 mg. of *m*-cresol
3. 0.6 mg. of phenol
4. 0.5 mg. of *o*-cresol

phenols extracted with diethyl ether, the ether extracts concentrated to a small volume by evaporation, the phenolic residue dissolved in acetic acid, and the color development carried out by the direct procedure. However, this procedure gave results which were generally about 3% low, indicating incomplete recovery of the phenols.

A variety of caustic solutions were tried as possible extractants for the phenols. None showed any definite advantage over the 10% potassium hydroxide solution initially decided upon. Generally, very concentrated solutions interfered with the color development by precipitating a large amount of salts when the alcohol was added. Modification of the recommended extraction procedure may be required in instances where the samples contain highly substituted alkyl phenols which are not easily extractable by 10% potassium hydroxide solution.

The application of the direct procedure to hydrocarbon samples was found to give low, erratic results even when the sample contained relatively high phenol concentrations. Evidently the acetic acid–potassium acetate solution failed to extract the phenols quantitatively or the color complex was soluble in the insoluble hydrocarbon layer which had to be removed by filtration.

Color Development Procedure. The most critical variable factors involved in the color development procedure were studied to determine their possible effect on the reproducibility of the method and to discover their optimum values. The composition of the reaction medium is an important factor. Variations in the concentration of either water or inorganic salts may have appreciable effects upon the intensity of the color of the final solution. The magnitude of these effects is indicated by the data of Table III. With most phenols variations in water content produced the least effect when 10 to 40% water was initially present; consequently, 20% water seemed most desirable. For the sake of uniformity and convenience the composition of the reaction medium was standardized at the composition corresponding to that obtained in the extraction procedure by diluting the accumulated caustic and water extracts to 100 ml. with glacial acetic acid. Under the conditions of the test the presence of the potassium acetate gave no undesirable effects and did not materially change the color intensity.

For the standard reaction mixture volume of 5 ml. it was found that the quantity of concentrated sulfuric acid could be varied between 3 and 12 drops without noticeable effect; similarly, the volume of saturated sodium nitrite solution could be varied between 1 and 4 drops without changing the result. The quantity of ammonia finally added to the reaction mixture was without effect on the color intensity, provided this amount was at least 175% of that required for neutralization of the acids present. However, different color intensities were produced if care was not taken to keep the mixture cool while neutralizing with ammonia.

The time of standing of the reaction mixture (after addition of the sulfuric acid and sodium nitrite) before neutralization with

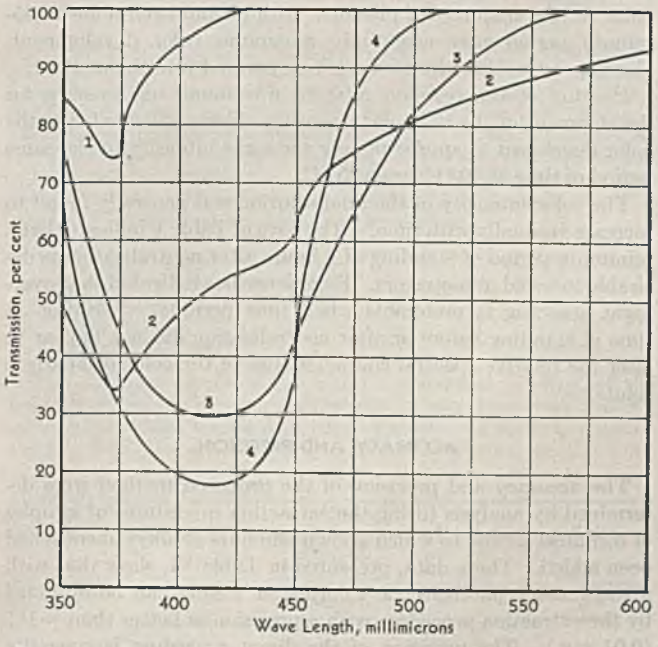

Figure 4. Spectral Characteristics of Color Comparison Solutions for Phenols and Phenolic Mixtures

Instrument, Coleman spectrophotometer, Model 10S
Cell depth, 13 mm. (square)

1. Reagent blank
2. 0.5 mg. of hydroquinone
3. 0.62 mg. of petroleum cresylic acid (b.r. 220–225° C.)
4. 0.5 mg. of resorcinol

Table IV. Influence of Time of Standing before Neutralization on Intensity of Color Produced by Phenols

Phenol present	Weight, Mg.	Net Colorimeter Reading for Indicated Time of Standing before Neutralization[a] 5 min.	10 min.	20 min.	30 min.	40 min.
Phenol	0.20	78.2	114.0	176.5	190.0	196.0
Phenol	0.80	313	495	560	564	580
o-Cresol	0.20	211.0	211.0	213.0	213.0	213.0
p-Cresol	0.20	90.0	92.0	92.0	92.0	92.0
p-Cresol	1.20	540	540	553	553	553
m-Cresol	0.20	162.0	156.0	142.0	142.0	142.0
Petroleum cresylic acid						
Boiling range 200–220° C.	0.20	147.0	148.0	137.5	137.0	132.0
200–225° C.	0.20	136.0	136.0	128.0	128.0	121.0
220–225° C.	0.20	98.8	97.5	93.4	88.2	82.5
220–225° C.	1.20	582	582	535	529	506
220–240° C.	0.20	79.0	79.0	80.0	73.0	73.0
235–290° C.	0.20	54.0	54.5	54.0	50.0	48.0

[a] All solutions allowed to stand 23 to 24 hours after neutralization before measuring color intensity. All measurements with Klett-Summerson photoelectric colorimeter.

Table V. Influence of Time of Standing after Neutralization on Intensity of Color Produced by Phenol Mixtures

Phenol Present	Weight, Mg.	Net Colorimeter Reading for Indicated Time of Standing after Neutralization[a] 0 hour	0.25 hour	1 hour	4 hour	24 hour
Petroleum cresylic acids						
Boiling range 220–225° C.	1.06	0.448	0.460	0.471	0.482	0.484
200–220° C.	1.03	0.602	0.613	0.623	0.629	0.633
200–225° C.	0.97	0.539	0.544	0.559	0.560	0.570
200–235° C.	1.16	0.549	0.558	0.565	0.576	...
220–240° C.	1.03	0.360	0.363	0.371	0.378	0.382
225–245° C.	1.01	0.360	0.363	0.371	0.372	0.383
235–290° C.	1.03	0.260	0.258	0.259	0.259	0.258

[a] All solutions allowed to stand 15 minutes before neutralization. All measurements made by Spekker photoelectric absorptiometer.

ammonia had an important bearing upon the color intensity of the final solution. In Table IV are summarized data showing the observed effects with samples of various phenols when the time of standing before neutralization was varied, other factors being maintained constant. There was no definite trend observed in the time range studied. However, a 15- to 30-minute period of standing before neutralization gave a fairly constant intensity of color for the majority of phenols; with phenol itself a 30- to 45-minute period gave essentially maximum color development. Consequently, these limits were incorporated into the method.

Heating of the reaction mixture was found unnecessary for development of the full color intensity. Tests indicated that the color developed to approximately the same intensity in the same period of time at 40° C. as at 25° C.

The color intensity of the final solution was generally found to increase gradually with time. The data of Table V indicate that a minimum period of standing of 4 hours after neutralization is desirable to avoid minor errors. Experience has indicated that overnight standing is preferable when time permits. Variation in time of standing before or after neutralization did not appear to alter the relative spectral characteristics of the color comparison solutions.

ACCURACY AND PRECISION

The accuracy and precision of the proposed method were determined by analysis (using the extraction procedure) of samples of technical octane to which known amounts of alkyl phenols had been added. These data, presented in Table VI, show that with a satisfactory photoelectric colorimeter results can be obtained by the extraction procedure with a precision of better than ±1% (0.01 mg.). The precision of the direct procedure is generally limited by the repeatability of the photoelectric colorimeter used; with a sensitive colorimeter and selective light filter a precision of ±0.5% (0.005 mg.) is generally obtained.

The systematic error is less than 2% of the actual concentration and is generally a negative error. However, the accuracy of the method is dependent largely upon choosing as a standard a phenol material which closely corresponds to that present in the sample being analyzed.

DISCUSSION

The proposed method has been found applicable to the determination of naphthols, monohydroxyphenols, and dihydroxyphenols in a large variety of substances; very few nonphenolic compounds interfere with the method. Through use of either the direct or extraction procedure satisfactory analyses have been obtained with many different types of samples, including gasoline, kerosene, fuel oil, thinners, hydrocarbon solvents, naphthenic acids, concentrated phenols, alcohols, polymers, chemical preparations, aqueous treating solutions, and other similar materials.

With samples containing a phenol or a mixture of phenols which has been partially identified the proposed method will give results with accuracy and precision comparable to most photoelectric methods. As a method for the analysis of a complex group of phenolic compounds, such as those occurring in petroleum products, the accuracy of the method depends upon the proper choice of standard. In most cases the results need only be relatively accurate, a condition which can be realized by use of an arbitrarily chosen standard such as pure phenol or *o*-cresol. In cases where the identity of the phenol is unknown yet accurate results are needed, it is necessary to isolate a small quantity of the phenol or phenol mixture. With aqueous solutions this can be accomplished by adjusting the solution to contain a slight excess of strong base (pH 12), filtering, adjusting the filtrate to the phenolphthalein end point (pH 8.5), and separating the phenols by centrifuging. With nonaqueous solutions, a quantity of sample is extracted with caustic solution and the phenols are sprung from the extract in the manner described.

Since only a few milligrams of the concentrated phenol mixture are required and quantitative recovery is not essential, isolation

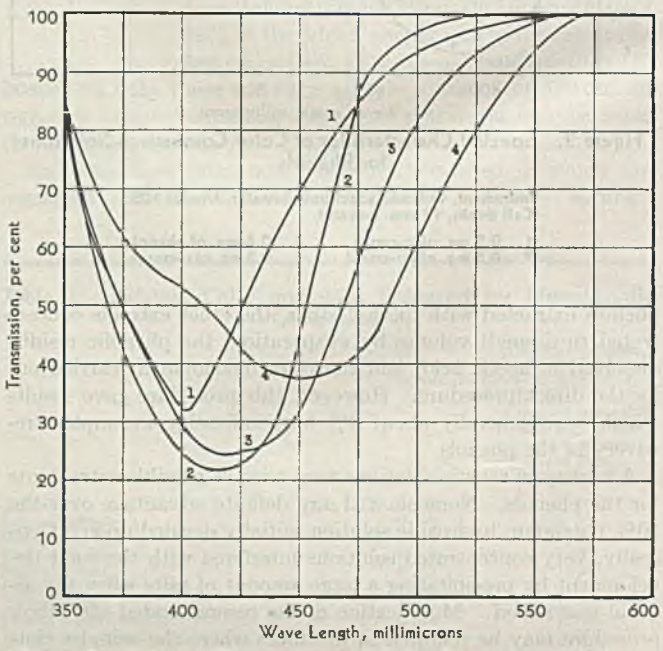

Figure 5. Spectral Characteristics of Color Comparison Solutions for Isomeric Dimethyl Phenols

Instrument, Coleman spectrophotometer, Model 10S
Cell depth, 13 mm. (square)

1. 0.58 mg. of 3,5-dimethylphenol
2. 0.54 mg. of 2,5-dimethylphenol
3. 0.54 mg. of 2,3-dimethylphenol
4. 0.54 mg. of 2,4-dimethylphenol

Table VI. Accuracy and Precision of Proposed Method

Petroleum Cresylic Acids (B.R. 220–225° C.) Added	Cresylic Acids Found[a]	Recovery
Mg./100 ml. technical octane	*Mg.*	%
0.0	0.0	
10.6	10.5	98.8
10.6	10.4	97.9
10.6	10.3	97.2
10.6	10.3	97.2
10.6	10.5	98.8
10.6	10.5	98.8
	Systematic error	−1.9
	Standard deviation	±0.7
92.2	92.4	100.2
92.2	92.2	100.0
92.2	90.9	98.6
92.2	91.5	99.2
92.2	90.8	98.5
92.2	91.3	99.0
	Systematic error	−0.7
	Standard deviation	±0.6

[a] Spekker photoelectric absorptiometer.

of the phenols presents only a minor problem. In any application it must always be realized that the colorimeter response per milligram of phenol is a specific property of that phenol or phenol mixture only—that is, the amount of color produced by the various phenols varies markedly. Accuracy of the method will depend upon the proper choice of a standard.

The experimental work reported in this paper demonstrates the wide scope and versatility of the method. It has found extensive use in research, control, and specification analytical work involving various types of materials and phenolic compounds.

ACKNOWLEDGMENT

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Analysis of Ternary Mixtures of Methylcyclohexane-Toluene-Aniline

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A method of analyzing the ternary mixture methylcyclohexane-toluene-aniline has been developed. The refractive index of the ternary mixture and of the residual binary hydrocarbon after removing the aniline by acid extraction completely defines the ternary system. With the aid of an experimentally established curve, the ternary analysis can be found.

THE analysis of a binary liquid mixture can often be made by measuring one physical property such as refractive index or density, when a second variable such as temperature is fixed. The introduction of a third component complicates the problem and necessitates fixing another variable to permit analysis by the measurement of one physical property. Unfortunately, fixing another variable is not easy, since both temperature and pressure (1 atmosphere) have already been fixed for the two-component system.

Varteressian and Fenske (*2*) analyzed mixtures of *n*-heptane–methylcyclohexane-aniline by means of refractive index measurements for the special case of liquid-liquid extraction where the solution was saturated and in equilibrium with a second immiscible solution at a given temperature and pressure, and also applied this method to the system benzene–ethyl alcohol–water (*1*) under the same conditions. The method of analysis described in this paper is concerned with the case where the solution is not saturated under specified conditions, but exists as a completely miscible solution.

PROPERTIES OF MATERIALS USED

The methylcyclohexane was the best commercial grade furnished by the Rohm and Haas Company of Philadelphia. It was extracted with concentrated sulfuric acid, washed, dried, and then fractionated in a laboratory column of approximately 35 theoretical plates. The best cuts from the fractionation were combined and used in this work. The purified material had the following properties:

50% boiling point at 760 mm., ° C.	100.90
0 to 50% boiling point spread, ° C.	0.0
Density, d_4^{20}	0.7695
Refractive index, n_D^{20}	1.42310

The toluene was also purified before use. The best commercial grade of nitration toluene furnished by the Barrett Company, Frankford, Pa., was fractionated in a large column of approximately 75 theoretical plates. The best cuts from the fractionation were sulfonated with concentrated sulfuric acid and separated from impurities by steam-distillation, after which the toluene was regenerated by hydrolysis. The regenerated toluene was then first fractionated to remove any by-product of hydrolysis. The purified material had the following properties:

50% boiling point at 760 mm., ° C.	110.65
0 to 50% boiling point spread, ° C.	0.0
Freezing point, ° C.	−95.2
Density, d_4^{20}	0.8672
Refractive index, n_D^{20}	1.49685

The aniline was the water-white commercial product of the Dow Chemical Company. Before use, it was dried over Baker's sodium hydroxide pellets and then subjected to three successive simple distillations, discarding a generous portion of the fore-

Table I. Analysis of Mixtures of Methylcyclohexane-Toluene-Aniline

(Using refractive index of binary hydrocarbon mixture and of ternary mixture)

	Composition of Test Mixtures, Weight Per Cent								
	Gravimetric Composition			By Analysis			Per Cent Error		
	M[a]	T	A	M	T	A	M	T	A
1	8.24	36.80	54.95	8.3	37.1	54.6	+0.73	+0.81	−0.64
2	20.90	23.52	55.60	20.8	23.4	55.8	−0.48	−0.51	+0.36
3	33.80	9.60	56.70	33.4	9.3	57.3	−1.18	−3.13	+1.06
4	13.20	14.85	71.90	13.1	14.6	72.3	−0.76	−1.68	+0.56
5	36.70	40.70	22.60	36.8	40.4	22.8	+0.27	−0.74	+0.88

[a] M = methylcyclohexane, T = toluene, A = aniline.

[1] Present address, Standard Oil Development Company, Linden, N. J.
[2] Present address, General Electric Company, Schenectady, N. Y.

Table II. Composition of Hydrocarbon Portion of Ternary Mixtures, Methylcyclohexane-Toluene-Aniline

(Expressed as mole per cent methylcyclohexane on a binary hydrocarbon basis)

Gravimetric Composition	Composition by Refractive Index, Analysis after Removal of Aniline by Dilute HCl[a]	Per Cent Error
17.4	17.5	0.57
45.5	45.4	−0.22
76.75	77.1	0.46
45.2	45.5	0.66
45.9	46.05	0.33

[a] One volume of concentrated hydrochloric acid diluted to 5 volumes with distilled water.

runnings and the residue. The purified aniline had the following properties:

Density, d_4^{20}	1.0219
Refractive index, n_D^{20}	1.5863

Since the system being analyzed consists of one phase and three components, the phase rule, $P + V = C + 2$, indicates that there are four variables. Two variables, temperature and pressure, can be easily fixed. When a third variable is fixed, measurement of a fourth variable will define the system. The third variable fixed is the ratio of methylcyclohexane to toluene or the composition of the hydrocarbon portion of the mixture on a solvent-free basis.

Table III. Refractive Index *vs.* Composition of Methylcyclohexane-Toluene-Aniline Mixtures with Mole Per Cent Methylcyclohexane in Toluene as Parameter[a]

Wt. % Aniline	n_D^{20} Ternary Mixture	Wt. % Aniline	n_D^{20} Ternary Mixture
0.0 Mole %[a]		9.9 Mole %	
0.00	1.4969	0.00	1.4874
10.40	1.5048	9.96	1.4957
20.80	1.5132	20.20	1.5048
31.35	1.5226	29.70	1.5136
40.60	1.5306	40.80	1.5241
50.40	1.5394	50.35	1.5334
60.30	1.5486	60.70	1.5439
70.70	1.5581	69.90	1.5535
80.20	1.5669	80.15	1.5664
20.2 Mole %		30.3 Mole %	
0.00	1.4784	0.00	1.4700
10.20	1.4880	11.46	1.4809
20.70	1.4981	20.25	1.4897
30.30	1.5076	30.20	1.5002
40.40	1.5181	40.40	1.5115
50.85	1.5291	51.20	1.5235
60.55	1.5398	60.10	1.5343
70.40	1.5512	70.50	1.5470
77.30	1.5582	80.20	1.5591
40.0 Mole %		49.05 Mole %	
0.00	1.4621	0.00	1.4552
10.23	1.4730	10.50	1.4660
19.98	1.4831	20.15	1.4769
29.95	1.4944	29.90	1.4888
40.50	1.5070	40.45	1.5020
50.60	1.5188	50.65	1.5140
59.80	1.5300	61.50	1.5289
70.00	1.5440	70.70	1.5418
80.30	1.5586	79.80	1.5550
59.4 Mole %		70.1 Mole %	
0.00	1.4479	0.00	1.4408
9.90	1.4583	10.20	1.4520
19.70	1.4698	29.80	1.4762
30.25	1.4824	26.45	1.4722
40.40	1.4958	40.70	1.4905
50.10	1.5090	50.60	1.5046
60.20	1.5232	60.40	1.5191
70.20	1.5380	69.20	1.5335
80.60	1.5545	80.20	1.5515
78.4 Mole %		90.0 Mole %	
0.00	1.4355	0.00	1.4285
10.90	1.4472	10.50	1.4400
19.50	1.4580	20.40	1.4505
30.30	1.4720		
40.50	1.4865	Phase separation occurred here	
49.80	1.5000		
69.90	1.5325		
79.90	1.5494		

[a] Mole % methylcyclohexane in toluene on binary basis.

ANALYTICAL PROCEDURE

The refractive index, n_D^{20}, of the ternary mixture is read. The aniline is then removed from the mixture by extraction with dilute hydrochloric acid (1 volume of concentrated acid diluted to 5 volumes with distilled water). The refractive index, n_D^{20}, of the hydrocarbon after this extraction is also read. From the latter datum, the composition of the hydrocarbon mixture can be obtained by means of a refractive index–composition chart. This composition and the refractive index of the ternary mixture are used in conjunction with the curves in Figure 1 to obtain the weight per cent of aniline in the ternary mixture. From this value and the composition of the hydrocarbon portion of the mixture, the over-all composition is calculated.

To check the accuracy of this method of analysis, five mixtures of methylcyclohexane-toluene-aniline were made up gravimetrically and analyzed. The gravimetric analyses and the experimental analyses of the mixtures are listed in Table I. The percentage error is based upon the gravimetric analysis as correct. Examination of the analyses shows good agreement in most cases, while no value is greatly in error.

Two sources of error exist in these analyses: the accuracy with which the refractive index of the ternary mixture can be read, and the accuracy of the hydrocarbon analysis after the aniline has been removed by dilute hydrochloric acid extraction. A study of the data in Table II will show that in almost every case the accuracy of the hydrocarbon analysis is within the accuracy of the refractive index measurements. Here again the percentage error is based upon the gravimetric composition.

The technique employed in obtaining the curves in Figure 1 was as follows:

A binary hydrocarbon mixture of methylcyclohexane-toluene of known composition was weighed out and combined with weighed amounts of aniline. The refractive indexes of these mixtures were read and a curve of refractive index versus weight per cent aniline was plotted with mole per cent methylcyclohexane in the binary hydrocarbon mixture as parameter. Ten points were obtained to establish each curve, and nine such curves were deter-

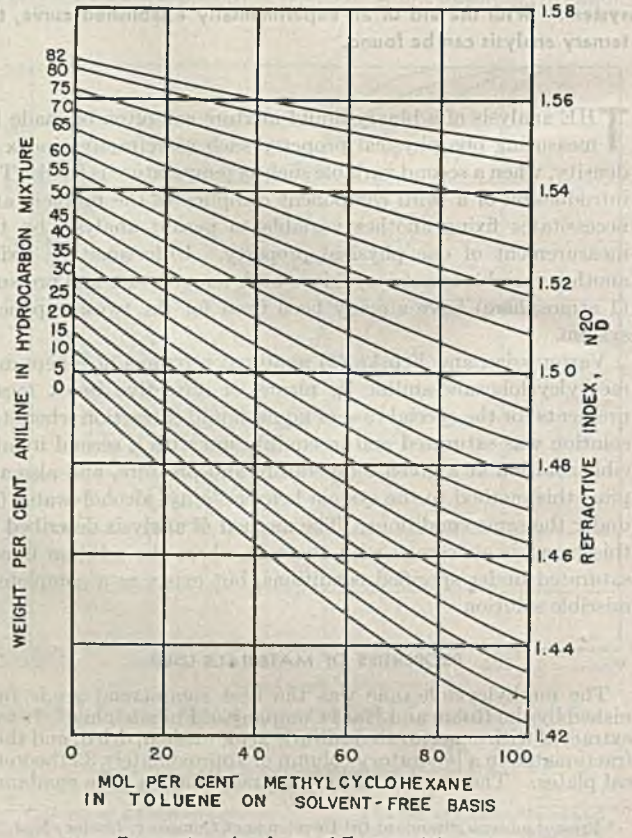

Figure 1. Analysis of Ternary Mixtures

Table IV. Refractive Index, Mole Per Cent Hydrocarbon Composition Data for Figure 1 for System Methylcyclohexane-Toluene-Aniline

Mole % Methylcyclohexane[a] / Wt. % aniline in ternary	0	9.9	20.2	30.3	40.0	49.05	59.4	70.1	78.4	90.0
	Refractive Index of Ternary Mixture									
0	1.4969	1.4874	1.4784	1.4700	1.4621	1.4552	1.4479	1.4408	1.4355	1.4285
5	1.5006	1.4914	1.4831	1.4747	1.4671	1.4601	1.4530	1.4461	1.4406	1.4337
10	1.5045	1.4957	1.4878	1.4795	1.4723	1.4653	1.4585	1.4517	1.4462	1.4394
15	1.5085	1.5000	1.4926	1.4845	1.4777	1.4709	1.4642	1.4577	1.4522	1.4455
20	1.5125	1.5046	1.4974	1.4896	1.4831	1.4767	1.4701	1.4639	1.4585	1.4522
25	1.5168	1.5091	1.5024	1.4947	1.4887	1.4827	1.4761	1.4700	1.4650	....
30	1.5211	1.5138	1.5073	1.4999	1.4944	1.4889	1.4823	1.4765	1.4717	....
35	1.5255	1.5185	1.5124	1.5053	1.5000	1.4950	1.4887	1.4829	1.4786	....
40	1.5300	1.5233	1.5175	1.5108	1.5059	1.5013	1.4953	1.4895	1.4857	....
45	1.5345	1.5281	1.5227	1.5164	1.5119	1.5076	1.5020	1.4964	1.4929	....
50	1.5391	1.5330	1.5281	1.5221	1.5181	1.5140	1.5088	1.5037	1.5004	....
55	1.5437	1.5381	1.5336	1.5280	1.5243	1.5205	1.5158	1.5111	1.5081	....
60	1.5483	1.5432	1.5392	1.5340	1.5308	1.5271	1.5229	1.5188	1.5160	....
65	1.5528	1.5483	1.5449	1.5401	1.5373	1.5339	1.5302	1.5267	1.5242	....
70	1.5574	1.5537	1.5506	1.5463	1.5441	1.5409	1.5377	1.5348	1.5326	....
75	1.5620	1.5589	1.5564	1.5526	1.5509	1.5480	1.5455	1.5429	1.5410	....
80	1.5667	1.5641	1.5622	1.5589	1.5578	1.5553	1.5534	1.5512	1.5496	....
82	1.5686	1.5663	1.5645	1.5615	1.5605	1.5583	1.5565	1.5545	1.5531	....

[a] Composition of hydrocarbon mixture on binary basis.

mined. Curves were easily fitted to the experimental points which are given in Table III. Since the weight per cent aniline was the desired parameter in this work, a cross plot was made, taking points from the curves at each 5 weight per cent aniline. These data, given in Table IV, provided nine points to establish each curve in Figure 1.

The curves in Figure 1 are not straight lines as is sometimes assumed. Charts similar to Figure 1 can be constructed completely on a mole basis or on a weight basis by converting the data in Table IV to the desired values.

ACKNOWLEDGMENT

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CONCLUSIONS

Ternary mixtures of methylcyclohexane-toluene-aniline can be analyzed rapidly and with good accuracy by reading the refractive index of the ternary mixture, followed by reading the refractive index of the hydrocarbon portion of the mixture after the aniline has been removed.

The same procedure may be useful for analyzing other types of hydrocarbon-solvent systems.

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Rapid Photometric Determination of Iron in Aluminum Alloys

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A method for the photometric determination of iron in aluminum alloys is based on the reaction of ferrous iron and 1,10-phenanthroline. The information given in this report is concerned with the formation, stability, and reproducibility of the reaction of ferrous iron and 1,10-phenanthroline. The method is rapid and the accuracy obtained is ±0.05% of the amount present.

A NUMBER of papers (*1*, *3*, *5*, *7*) have described the use of 1,-10-phenanthroline in the photometric determination of iron in foods, iron ores, and biological materials.

Smith and Richter summarized work done with 1,10-phenanthroline up to 1944 (*6*).

Blau gave a description of the properties of 1,10-phenanthroline along with the method of preparation (*1*). Walden, Hammett, and Chapman showed that the complex ion formed with ferrous iron and 1,10-phenanthroline has a high oxidation potential and may be used as an indicator in certain oxidimetric procedures (*7*). Saywell and Cunningham developed a photometric method for determining small amounts of iron in fruit juices (*5*). In the field of metallurgical analysis, Mehlig and Hulett described a method for the photometric determination of iron in iron ores (*3*).

The purpose of the work described in this paper was the development of a rapid and accurate method for the determination of iron in aluminum alloys based upon the formation of ferrous phenanthroline complex.

EXPERIMENTAL WORK

The reaction of 1,10-phenanthroline and ferrous iron is the basis for the work described in this paper. At the time of the investigation, there were no known published papers describing the use of 1,10-phenanthroline in the determination of iron in aluminum alloys.

The reaction of 1,10-phenanthroline and ferrous iron produced an orange colored solution, the color intensity varying with the iron content.

Methods for dissolving aluminum were investigated. Hydrochloric acid (1 to 1) was found to be the best solvent for this purpose; it also aided in the removal of interfering ions, which are insoluble in hydrochloric acid. If sodium hydroxide were used, hydroxylamine hydrochloride when added would act as an oxidizer of iron instead of a reductant (*4*).

The following were the available reductants: 10% aqueous solution of hydroxylamine hydrochloride, 0.25 molar solution of stannous chloride, 10% solution of sodium sulfite, formaldehyde, and hydroquinone. The 10% solution of hydroxylamine hydrochloride proved to be the best, as appreciable errors showed up when the other reductants were used. This was due to the complexes formed with iron which kept the 1,10-phenanthroline from reacting completely with it.

All spectrophotometric measurements were made with the Coleman Universal spectrophotometer Model 11; the cell thickness for this instrument is 13 mm. For routine work the Fisher AC Model electrophotometer may be used with a filter of 490 mμ; the cell thickness is 23 mm.

To determine the wave length which would produce the maximum absorption, a representative concentration of the solution was examined at a series of wave lengths. The peak of absorption when using the Coleman spectrophotometer is at 490 mμ. The representative sample used contained 0.50% iron.

A series of photometric measurements showed that 15 minutes after the 1,10-phenanthroline was added the color became stable and remained so for at least 48 hours. The tests were discontinued at the end of this period.

Very few ions interfere with the determination of iron in aluminum alloys. Fortune and Mellon made an exhaustive general study of ions which interfere with the reaction of ferrous iron and 1,10-phenanthroline. The writer found that silicon, copper, and bismuth interfere with the determination of iron in aluminum alloys (*2*), but these elements are insoluble in hydrochloric acid and, therefore, can be removed by filtration. Zinc forms a precipitate with 1,10-phenanthroline. With small amounts of zinc, it was possible to prevent appreciable interference by adding a slight excess of 1,10-phenanthroline. Unless the concentration of zinc was greater than 10 parts per million it caused no appreciable error. The absence of interfering ions makes the method ideal for rapid, routine work.

REAGENTS REQUIRED

Hydrochloric Acid (1 to 1), 1000 ml. of distilled water and 1000 ml. of C.P. hydrochloric acid (specific gravity 1.19).

Hydroxylamine Hydrochloride (10%). Dissolve 10 grams of C.P. hydroxylamine hydrochloride crystals in 100 ml. of distilled water. (Store in refrigerator. Do not use if the solution has a brown color.)

1,10-Phenanthroline (0.25%). Dissolve 0.500 gram of C.P. 1,10-phenanthroline monohydrate crystals in 150 ml. of boiling distilled water. Cool, transfer to a 200-ml. volumetric flask, and dilute with distilled water. (Store in refrigerator. Do not use if the solution has a brown color, as this indicates decomposition.)

Standard Iron Solution. Dissolve 1.000 gram of pure iron wire in 50 ml. of concentrated hydrochloric acid. Transfer to a 1000-ml. volumetric flask. Dilute to the mark with distilled water (1 ml. = 0.1% iron or 0.001 gram of iron).

Table I. Comparison of 1,10-Phenanthroline Photometric Method and Other Methods

Sample No.	Other Methods[a]	1,10-Phenanthroline Photometric Method
	%	%
114B	0.66	0.66
85	0.38	0.39
86B	1.52	1.53
4064	0.33	0.33
3044	0.68	0.67
2624	0.80	0.80
9193	0.32	0.33
N1218	0.98	0.98
N1223	1.02	1.00

Each value is an average of 12 determinations.

[a] Permanganate and dichromate methods.

METHOD

Dissolve a 0.500-gram sample of aluminum in 30 ml. of hydrochloric acid (1 to 1), using a 250-ml. beaker and heating if necessary. Filter into a 500-ml. volumetric flask, using Whatman No. 41 filter paper. Wash five times with hot distilled water, cool, and dilute to mark with distilled water. Pipet 10 ml. of solution into a 100-ml. volumetric flask if the sample contains up to 0.50% iron. Pipet 5 ml. of solution into a 100-ml. volumetric flask if the sample contains over 0.50% iron. Add 1 ml. of hyroxylamine hydrochloride (10%) and mix. Add approximately 70 ml. of distilled water and mix. Add 10 ml. of 1,10-phenanthroline (0.25%) and mix. Dilute to the mark with distilled water, shake thoroughly, and let stand for at least 15 minutes. Using the Coleman spectrophotometer, set the wave length dial at 490 and measure the color density of the solution. If a Fisher electrophotometer is used, a 490 mμ filter is required. Use distilled water as reference solution.

A shortage of standard samples made it necessary to develop a method by which a pure iron solution could be used. This was possible because of the absence of interfering elements. A 1.000-gram sample of pure iron wire was dissolved in 50 ml. of concentrated hydrochloric acid, then transferred to a 1000-ml. volumetric flask and diluted to the mark with distilled water (1 ml. = 0.1% iron or 0.001 gram of iron).

All results obtained in this study were calculated on the basis of a pure iron solution standard (Table I). The percentage error was approximately ±0.05% of the amount present.

Beer's law was followed by the color system, as shown by the straight line obtained when the readings of the observed transmittancies at 490 mμ for the solution containing up to 5.00% iron were plotted logarithmically.

DISCUSSION

The formation of the complex when ferrous iron reacts with 1,10-phenanthroline is represented by the radical: $(C_{12}H_8N_2)_3$-Fe^{++}. This is an orange-colored compound, formed when 1 molecule of ferrous iron combines with 3 molecules of 1,10-phenanthroline.

The basic reaction of hydrochloric acid and the sample does not form any ferric iron, but, upon heating, some of the ferrous iron may be converted to the ferric state. The addition of the reductant, hydroxylamine hydrochloride, converts this ferric iron to ferrous. The reverse occurred when the sample of aluminum was dissolved in sodium hydroxide; instead of hydroxylamine hydrochloride acting as a reductant, it became an oxidizer of iron. This method compares favorably with other methods of determining iron in aluminum alloys.

An important advantage over other photometric methods for determination of iron is that the pH need not be regulated closely. However, the ferrous color will not develop at a pH much below 2, and the reduction of iron with hydroxylamine is slow at a pH much above 3. The color formation occurs in the acid solution, eliminating the difficulties usually caused by precipitation of metal hydroxides and hydrated oxides in alkaline solution. Another advantage is freedom from interference of diverse ions.

SUMMARY

The reaction of 1,10-phenanthroline and ferrous iron produces an orange-colored complex. Any ferric iron present is reduced with hydroxylamine hydrochloride.

Very few ions interfere with the color reaction. Silicon, copper, and bismuth are the most common elements present in aluminum alloys which interfere with the formation of the ferrous-phenanthroline complex, but they are eliminated by filtration because they are insoluble in the solvent for aluminum.

Tests prove that the color reaction is stable for at least 48 hours, thus confirming the observations of other workers.

The wave length of 490 mμ produces the maximum absorption of these instruments.

Representative samples, analyzed and plotted logarithmically, prove Beer's law holds for the concentrations employed.

An accuracy of ±0.05% is possible with this method. It is more rapid than the standard volumetric or gravimetric methods for determining iron in aluminum alloys.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Richard B. Faurote, chief chemist, for his interest and helpful criticism during the development of this method.

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Chemical Determination of Vitamin A in Dried Whole Eggs

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A chemical method is described for the determination of vitamin A in dried whole eggs by the use of chromatographic adsorption. After the sample is hydrolyzed with alkali and extracted with ethyl ether, the unsaponifiable fraction is adsorbed on a column of calcium hydroxide and the β-carotene, cryptoxanthol, vitamin A, luteol, and zeaxanthol bands are allowed to separate. The provitamins are eluted and determined separately. Antimony trichloride reagent is then added to the combined vitamin A and provitamin A eluates and the amount of blue color determined in a photoelectric colorimeter. Data presented on nine samples of dried eggs show that the values obtained by the chemical method agree within 10% with those obtained by bioassay.

ATTEMPTS to use published chemical methods (*5*, *7*) for the determination of vitamin A in dried eggs in this laboratory failed to give values in agreement with those obtained by bioassay. Investigation showed that differences resulted from poor extractability of the vitamin and errors caused by the presence of large amounts of carotenols for which arbitrary corrections were not reliable.

When extraction of dried eggs in the Waring Blendor was tried as outlined in the method of Schrenk, Chapin, and Conrad (*7*), a large amount of vitamin A remained in the residue. The residue was hydrolyzed with alkali and extracted with ethyl ether, after which the light absorption of the extract was measured at 326 and 450 millimicrons. The values obtained indicated the presence of substantial amounts of both vitamin A and carotenoids. Values obtained by the Carr-Price reaction further substantiated the presence of vitamin A.

Bioassays of the extracted residue provided further proof that ethyl ether extraction of the whole egg does not remove vitamin A quantitatively. In this experiment about 200 grams of a dried egg sample were extracted with ethyl ether in a large Soxhlet extractor for 24 hours. The residue showed a biological potency equivalent to 14.5 I.U. of vitamin A per gram.

Various solvents were used in attempts to remove the vitamin A quantitatively. A 45-gram sample of dried egg was extracted with about 250 ml. of solvent in a Soxhlet extractor. To test the completeness of extraction, a sample of the residue was hydrolyzed with alkali, the unsaponifiable matter was extracted with ethyl ether, and the amount of vitamin A was determined by the Carr-Price reaction. The results (Table I) showed that ethyl ether was the poorest solvent of those tried for the extraction of vitamin A. However, the solvents which were most effective for the extraction had relatively high boiling points, and prolonged heating resulted in darkening of the extract.

Large amounts of carotenols in the dried eggs were shown to cause substantial errors when attempts were made to determine the vitamin A by means of the Carr-Price colorimetric procedure as modified by Koehn and Sherman (*5*). Klose, Jones, and Fevold (*4*) reported satisfactory agreement of results obtained by this method with those shown by bioassay. When this procedure was used with the total unsaponifiable extract the values were consistently higher than those with the bioassay procedure (Table III, column 3). Attempts to employ an arbitrary factor to correct for carotenoids were unsuccessful.

Reliable results were obtained by chromatographic separation of the unsaponifiable extract obtained after direct alkaline hydrolysis of the whole egg. Gillam and Heilbron (*2*) had shown that the vitamin A of egg yolk could be separated from xanthophylls by adsorption on calcium carbonate and elution with petroleum ether–benzene. However, no attempt at quantitative separation was made.

Preliminary trials in this laboratory revealed that calcium hydroxide was a better adsorbent than calcium carbonate for the chromatographic separation of the carotenoids of eggs. When the unsaponifiable extract was adsorbed from a petroleum ether solution and the column developed with a mixture of 60% benzene and 40% petroleum ether a sharp separation was obtained. The carotenoids were eluted from the column in the following order: β-carotene, cryptoxanthol, vitamin A, luteol, and zeaxanthol. The identity of β-carotene, cryptoxanthol, and luteol was established by comparing light absorption curves (Beckman spectrophotometer, Model DU) with the curves of the pure materials (*8*). The zeaxanthol band contained large amounts of isomerized material as indicated by comparison with a curve of pure zeaxanthol. The amounts of β-carotene, cryptoxanthol, and total carotenoids agreed well with the values obtained by Schrenk *et al.* (*7*) (Table III). A satisfactory light-absorption curve on the vitamin A eluate was not obtained. Contributing to this failure was a contaminant dissolved from the calcium hydroxide and Hyflo Super-Cel which absorbed in the region of 310 to 370 millimicrons. The presence of this material was shown by allowing the benzene–petroleum ether solution to run through fresh adsorbent and determining the light absorption of the percolate. This material gave no color with antimony trichloride but attempts to remove it completely before chromatographing were unsuccessful.

Preliminary attempts to determine vitamin A concentration by direct spectrophotometric measurements on the eluate were discouraging. This was consistent with the observations of Hauge, Zscheile, Carrick, and Bohren (*3*) who found that the curves given by the total carotenoids of fresh eggs as well as dried eggs were very different from that of vitamin A alcohol, both in position of maximum and in shape. Denton, Cabell, Bastron, and Davis (*1*) found they could not determine vitamin A in dried eggs spectrophotometrically because impurities absorbing in the region of the vitamin A maximum did not remain constant during storage.

Adsorption and elution of vitamin A from the calcium hydroxide chromatogram were shown to be satisfactory (Table II). Crystalline vitamin A alcohol and the unsaponifiable fraction from standard U.S.P. reference cod liver oil were used in these tests. In each case the vitamin was adsorbed from petroleum ether solution and eluted with benzene–petroleum ether. The solvent was removed from the eluate, the vitamin A redissolved in chloroform and treated with antimony trichloride reagent,

Table I. Efficiency of Solvents in Extraction of Vitamin A from Dried Whole Egg[a]

Solvent	Extraction Time *Hours*	Per Cent of Initial Weight of Egg Extracted	Vitamin A Content of Residue *I.U./gram*
Ethyl ether	30	38.0	9.3
	89	41.7	9.7
Ethyl alcohol	42	51.0	2.3
Absolute alcohol	89	51.5	2.3
80% benzene } 20% alcohol }	42	50.0	2.0
80% benzene } 20% absolute alcohol }	89	51.0	2.3
Carbon tetrachloride	94	43.9	2.0
1,2-dichloroethane	94	46.5	1.5
Trichloroethylene	42	45.5	3.7

[a] Vitamin A content by bioassay, 60 I.U. per gram.

[1] Present address, U. S. Army Medical Nutrition Laboratory, Chicago 9, Ill.

and the light transmission determined with an Evelyn photoelectric colorimeter. Further studies showed that vitamin A could be separated from luteol. This pigment followed vitamin A closely on the chromatogram.

METHOD

For the hydrolysis, a 5.0-gram sample is weighed into a 125-ml. Erlenmeyer flask, and 20 ml. of absolute methanol and 5 ml. of saturated aqueous potassium hydroxide are added. The contents are stirred with a glass rod until complete suspension of the sample is effected. The flask is then heated on a steam bath for 10 minutes or until the dried egg particles are disintegrated. The hydrolyzate is then cooled and transferred with 70 ml. of water to a 500-ml. separatory funnel. The first extraction is made with 35 ml. of peroxide-free ethyl ether and the four subsequent extractions with 25- to 30-ml. portions. The last extractions should be almost colorless. The ether extract is washed five times with 25-ml. portions of water, after which it is dried over 20 grams of anhydrous sodium sulfate for 1 hour at room temperature. The ether extract is evaporated to approximately 15 ml. under reduced pressure in a 50° C. water bath and then transferred to a 25-ml. volumetric flask with dry petroleum ether. If the solution still contains some moisture, as indicated by cloudiness, it should be dried with a small amount of sodium sulfate.

In the chromatographic separation 10 ml. of this solution are adsorbed on a column (20 × 135 mm.) of 3 parts of calcium hydroxide (Braun's Lot No. 10,588) and 2 parts of Hyflo Super-Cel. The chromatogram is developed with a mixture of 60% benzene (thiophene-free) and 40% dry petroleum ether. The two lowest bands containing β-carotene and cryptoxanthol are eluted separately. The vitamin A fraction is collected until the luteol begins to give a yellow color to the eluate. If the column is properly packed, the β-carotene and cryptoxanthol bands are easily distinguished. The luteol band should be sharp as it nears the bottom of the column. Fifty to 80 I.U. of vitamin A and 150 to 200 micrograms of total carotenoids (as β-carotene) can be handled satisfactorily with the column described. A total volume of 250 to 500 ml. of combined β-carotene, cryptoxanthol, and vitamin A eluate is the optimum range for best results.

Table II. Recovery of Vitamin A from a Calcium Hydroxide Chromatogram

Source of Vitamin A	Vitamin A Adsorbed	Vitamin A Eluted	Recovery
	I.U.	*I.U.*	%
U.S.P. reference cod liver oil No. 2	24	26	108
	122	115	95
	235	243	103
Crystalline vitamin A alcohol[a]	19.7	19.0	96
	20.3	18.5	91

[a] Purchased from Distillation Products, Inc.

After removing the solvent from the β-carotene and cryptoxanthol fractions, they are taken up in 10 ml. of petroleum ether and the light transmission is measured by means of the Evelyn photoelectric colorimeter with the standard 440 mμ filter. These solutions are then recombined with the vitamin A fraction and the solution is evaporated under reduced pressure at 50° C. to approximately 15 ml. This solution is then transferred to a 25-ml. volumetric flask with redistilled chloroform. Chloroform is used in this transfer because it is a somewhat better solvent than petroleum ether. Ten milliliters of this solution are evaporated to dryness in a colorimeter tube and redissolved in 2 ml. of chloroform. The tube is placed in the Evelyn instrument, 8 ml. of antimony trichloride reagent are added, and the light transmission is measured with the standard 620 filter. The blue color should be read within 5 to 10 seconds after the antimony trichloride reagent is added. This color should be brilliant and clear. Cloudiness in the solution at this point usually indicates insufficient care in excluding adsorbent or moisture.

One gram of U.S.P. reference cod liver oil No. 2 was saponified and extracted by the above procedure in establishing the calibration curve for the vitamin A. A sample of β-carotene, purified by chromatography, was used as the standard for the determination of β-carotene, cryptoxanthol, and total carotenoids.

RESULTS AND DISCUSSION

Results obtained on dried egg samples with this method were reproducible and showed good agreement with those obtained by bioassay (Table III). Eight samples of dried eggs of different storage history were tested for vitamin A by both methods with a maximum deviation of 10% in results. Eight replicate chemical determinations on a single sample showed similar reproducibility.

Several precautions were found necessary with respect to materials and procedure; other precautions were taken without testing their importance. One of the most important precautions to be observed in using this method is the preparation of the petroleum ether. Some samples of commercial petroleum ether contain an impurity which produces a green color when mixed with the antimony trichloride reagent. The use of such petroleum ether without purification results in erratic vitamin A values. The petroleum ether was purified as follows:

Four to five gallons of commercial petroleum ether (boiling point 65° to 67° C.) were percolated through a column (7 × 35 cm.) of silica gel (The Davison Chemical Corporation, No. 659,-528-2000). The percolate was then placed in a 5-gallon flask and stirred mechanically for several hours with each of two successive portions of concentrated sulfuric acid. The two phases were separated and the last trace of acid was removed by treatment with a dilute solution of sodium hydroxide. The petroleum ether was then stirred for a few hours with alkaline potassium permanganate, after which it was drawn off, distilled, and dried over anhydrous sodium sulfate.

Trouble was encountered with the adsorbent when the humidity in the laboratory became high. Under these conditions the carotenoids moved too rapidly down the column and it was impossible to separate the β-carotene and cryptoxanthol fractions. This difficulty was avoided by storing the adsorbent in a desiccator over sulfuric acid and removing it only long enough to pack the column.

Among the necessary operations was the addition of the β-carotene and cryptoxanthol fractions back to the vitamin A

Table III. Comparison of Chemical and Bioassay Methods[a]

	Chemical Methods							
	Not Chromatographed		Chromatographed				Bioassay, Vitamin A	I.U. (Chemical) / I.U. (Bioassay) × 100
Sample	Total carotenoids[b]	Vitamin A[c]	β-Carotene	Cryptoxanthol[b]	Vitamin A	Total vitamin A activity[d]		
	Micrograms/gram	*I.U./gram*	*Micrograms/gram*		*I.U./gram*		*I.U./gram*	
3B	100.6	71.4	3.0	3.2	39.0	46.7	44.0	106
4B	106.9	93.0	3.4	3.6	31.5	40.2	41.0	98
5B	102.0	75.5	4.3	4.8	30.7	41.9	43.0	98
8B	70.3	54.7	2.6	3.0	21.2	28.0	30.0	94
9B	114.0	82.0	3.3	3.3	30.2	38.5	41.0	94
10B	101.3	74.0	2.0	3.5	25.5	33.3	36.0	93
12B	79.5	65.0	2.5	2.7	26.0	32.4	32.0	101
13B	72.9	..	2.2	3.6	20.9	27.6	25.0	110
14	98.2	80.0	2.8[e]	3.4[e]	35.1	42.6	45.0	95
	94.5	..	..	..	37.0	44.5	..	99
	95.0	..	..	..	36.4	43.9	..	97
	97.6	..	..	..	36.1	43.6	..	97
	91.9	..	..	..	33.9	41.4	..	92
	97.7	..	..	..	36.8	44.3	..	98
	..	..	..	..	36.9	44.4	..	99
	95.7	..	..	..	33.4	40.9	..	91

[a] All values expressed on moisture-free basis.
[b] Expressed as β-carotene.
[c] Calculated from blue color given by total unsaponifiable extract.
[d] I.U. of vitamin A equivalent to 0.6 microgram of β-carotene and 1.2 micrograms of cryptoxanthol (6).
[e] Four determinations gave 2.8 and 3.4 as average values for β-carotene and cryptoxanthol, respectively, on this sample.

eluate before reacting with antimony trichloride, since it was found that small amounts of the vitamin were contained in these two eluates. This overlapping of vitamin A with the carotene and cryptoxanthol bands was not prevented by complete removal of the ether from the petroleum ether–ether solution of unsaponifiables before chromatographing. However, the bands were sharper when pure petroleum ether was used. β-Carotene and cryptoxanthol were shown experimentally to give only 7 and 11%, respectively, of the blue color given by vitamin A on reaction with antimony trichloride. Therefore, the effects of the β-carotene and cryptoxanthol on the total blue color development were so small as to be negligible. With one lot of eggs which was analyzed an additional small band was observed in the region of the β-carotene and cryptoxanthol bands. Depending upon the dietary constituents of the hen, still other bands might be expected. Should these occur in substantial amounts a correction would be necessary.

The following precautions were used without testing their importance.

Freshly distilled ethyl ether was used for extraction of the vitamin. Anhydrous ethyl ether (alcohol-free) was allowed to stand several days over potassium hydroxide and then redistilled. Chloroform (A.R.) was distilled over anhydrous potassium carbonate and stored in a brown bottle. The antimony trichloride reagent was made up by dissolving 22.5 grams of antimony trichloride in 100 ml. of redistilled chloroform, filtering, and storing in a brown bottle. A pipet calibrated to deliver 8 ml. and equipped with a rubber bulb for rapid delivery was used for adding the antimony trichloride reagent directly to the sample in the colorimeter tube. An all-glass distillation apparatus was used for the removal of solvent.

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Measuring Coverage and Film Thickness of Printing Ink and Paint Films

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THE determination of the amount of paint, lacquer, or printing ink on a given area of a certain surface—i.e., paper, metal, wood, or plastic—is of considerable interest in various technical fields. In the printing process, for example, it is desirable to print as thin a film as possible because this reduces, or eliminates completely, technical difficulties such as slow drying, offset, and fill-up in the half-tone plates, which are frequently encountered when it is necessary to use a greater film thickness. Similar considerations apply in the field of paint technology. Furthermore, the optical properties of a paint or printing ink film are closely related to the film thickness. Both the reflection and transmission spectra are functions of the film thickness. Hiding power depends essentially on the over-all absorption coefficient as a function of the wave length and the thickness of the particular specimen. The relationship between coverage and the actual structure to which the film is applied is another important problem in the paint and printing ink field.

Several methods have been described in the literature for measuring the coverage or the thickness of such films. One of the simplest procedures consists in weighing the specimen before and after application of the film-forming material. When applied to printing on paper this method is not satisfactory because an accurate weight determination (within 0.3 mg.) of a sheet of paper is impossible. This difficulty has been overcome (*2*) by using as a printing plate a very thin sheet of copper (or some other suitable metal) which is held firmly to a heavy base during the printing operation. The weight of the copper sheet before and after printing can easily be determined to within ±0.1 mg. Although the method in this form is very accurate, it has several drawbacks which limit its usefulness considerably. The film thickness can be determined only if the material is applied as described above; it is not satisfactory if a film-forming material containing some volatile matter is employed. An electrical method (*3*), based on capacity measurements, cannot be applied for measurements upon paper surfaces. Optical methods (*1*, *4*), based on interference patterns or on microscopic examination of microtome sections, are either not applicable to paper surfaces or too impractical to be useful.

Two methods developed in this laboratory overcome most of the difficulties mentioned above. Both methods make use of a tracer material which is added to the film-forming material. In one case the tracer material is a dyestuff, in the other a radioactive isotope. Although both methods were developed primarily to study the film thickness of printing inks, they are believed to be applicable to paints, lacquers, or other protective coatings.

METHODS

Dyestuff as Tracer Material. A known amount of dyestuff is added to a printing ink, and prints made from this ink are put into a Soxhlet extractor. Using alcohol, for example, it is possible to remove the dyestuff quantitatively from the print. The amount of dyestuff present in the alcohol solution is determined by measuring the transmission coefficient at a given wave length, following the standard procedure of quantitative colorimetric analysis.

To obtain satisfactory results the following factors should be carefully considered. The absorption spectra of the extraction and of the standard solutions (which furnish the calibration curve) must be identical, as shown in Figure 1, at least in the wave-length region where the colorimetric measurements are made. The presence of oils and resins in the extraction may in certain cases shift the absorption bands sufficiently to produce erroneous results. The extraction must be complete. This can easily be verified by repeated extractions or by a comparison of results obtained with the gravimetric method (*2*) and the dyestuff method, using the same prints in both cases. Data given in Table I, which are typical of a large number of printing inks, show that the extraction is complete. The absorption can also be disturbed by the presence of colloidal particles, such as carbon black pigments, which might produce a certain amount of turbidity. This point can easily be checked by running extractions

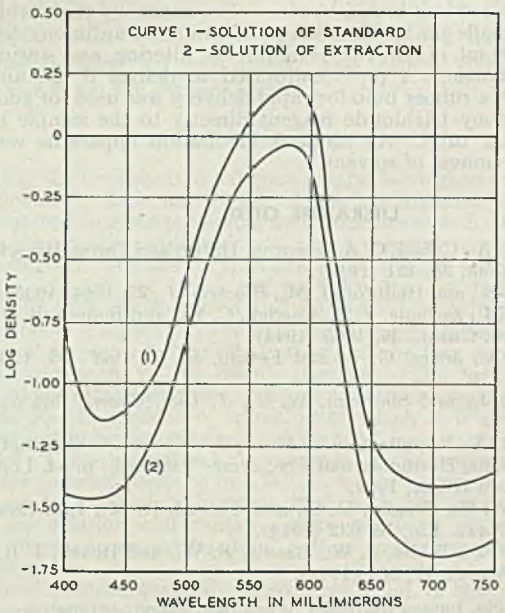

Figure 1. Log *D* Curves of Two Dyestuff Solutions

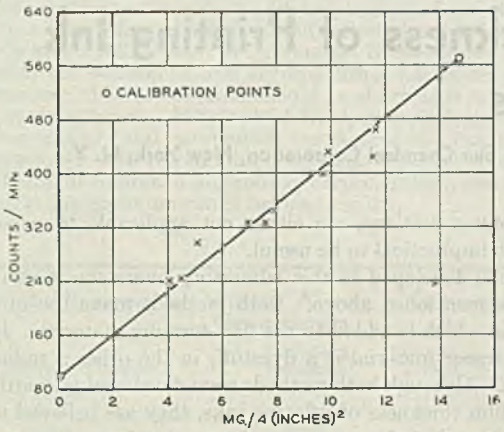

Figure 2. Counting Rate as a Function of Amount of Ink on a Given Print Area

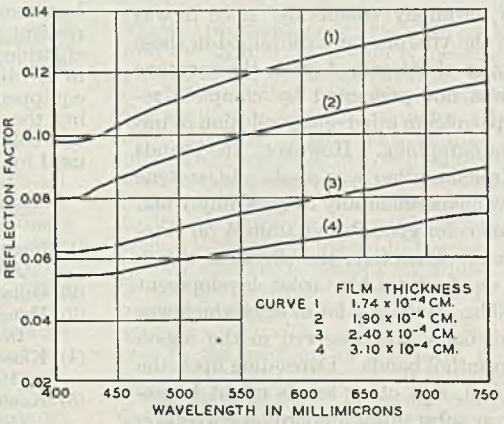

Figure 3. Reflection Spectrum of Prints of Different Film Thickness

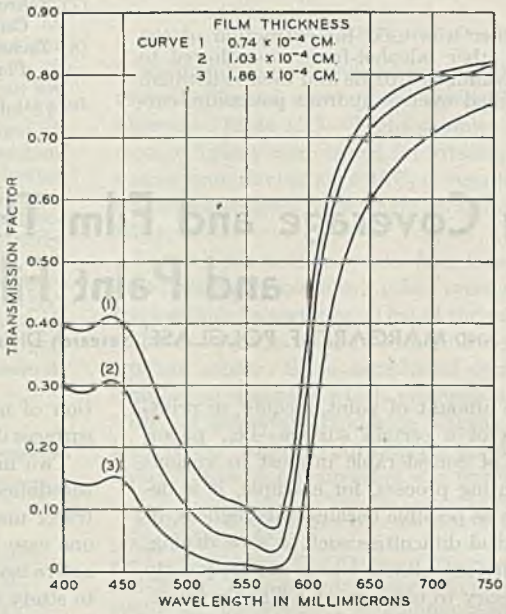

Figure 4. Transmission Spectrum of Prints of Different Thickness

on a printing ink containing no dyestuff. In this case the absorption spectrum of the extraction should be the same as, or at least very close to, the absorption spectrum of the solvent. Finally, it must be ascertained that the absorption spectrum of the dyestuff does not change irreversibly at the temperature at which the extraction is carried out. When all these factors are taken into account the results obtained by this method are judged to be accurate to at least ±7%.

RADIOACTIVE ISOTOPE AS TRACER MATERIAL. A known quantity of a radioactive compound (preferably a liquid) is added to a printing ink. Using the modified weighing method described above, a print is made with a known amount of ink on a given area of paper. The activity of this print is measured with a conventional Geiger counter set. (The instrument used in these experiments is built by the Cyclotron Specialties Corporation, Moraga, Calif.) This quantity and the background activity due to cosmic radiation give the calibration curve (Figure 2). The calibration curve changes with time because of the constant decay of the radioactive isotope.

In order to obtain satisfactory results the following points should be considered. The position of the counter tube relative to the sample must remain the same because the number of radioactive disintegrations picked up by the counter tube depends, among other things, on the geometry of the experimental setup. The radioactive material should be uniformly distributed throughout the printing ink. This can best be achieved by using a material which is miscible with the liquid phase of the printing ink. Finally, the activity of the specimen under test should be at least twice that due to the background radiation. An accuracy of ±3% can easily be obtained with this method.

Table I. Amount of Printing Ink on a Given Print Area

(Dyestuff used, methyl violet. Extraction solvent, alcohol. Extraction time, approximately 30 minutes per print)

Gravimetric Method	Dyestuff Method
Gram/25 sq. inches	
0.0521	0.0480
0.0283	0.0320
0.0331	0.0314
0.0310	0.0314
0.0430	0.0438
0.0380	0.0374

Table II. Amount of Ink on a Given Area of a Print for Different Papers

Machine Coated Paper	Amount of Ink
	Gram/sq. cm.
1	0.405×10
2	1.03×10^{-4}
3	1.21×10^{-4}
4	1.40×10^{-4}
5	2.5×10^{-4}

RESULTS

Table I gives comparative data obtained with the dyestuff and the gravimetric methods for a series of prints, using the same ink and paper. Table II shows the amount of ink taken up by various papers, keeping all other variables constant. The dyestuff method was used to obtain these data.

Figures 2, 3, and 4 show results using a radioactive isotope as tracer material. A radioactive isotope of phosphorus in the form of phosphorus pentachloride (obtained from the Radiation Laboratories, Massachusetts Institute of Technology) was used in these experiments. Figure 2 shows a comparison between the radioactive and the gravimetric methods. The scattering of some of the points on this graph is due to the nonuniform distribution

of the ink on the paper surface. For the gravimetric method the amount of ink per unit area was determined from a print area of 12.5 × 12.5 cm. (5 × 5 inches); the radioactive measurements, however, were made on a print area of 5 × 5 cm. (2 × 2 inches). Figure 3 shows the change of the reflection coefficient (measured with a GE recording spectrophotometer) as a function of the film thickness; Figure 4 shows the change of the transmission spectrum (between 400 and 700 millimicrons) of a printing ink printed on cellophane paper as a function of the film thickness.

There are limitations to both methods. Although the dyestuff method can be applied in many cases where the gravimetric method breaks down, it is still a relatively slow procedure. Furthermore, in many cases it might be undesirable or even impossible to incorporate a dyestuff into the material under consideration. The most important limitation with regard to the radioactive tracer method is that imposed by the radioactive decay of the isotope. The particular isotope in this work has a half-life of 15 days. Using a fairly strong preparation (60 microcuries per cc. of varnish) the coverage on an area of 25 sq. cm. (4 square inches) can be determined for a period of about 6 weeks. On the other hand, the advantages gained by the use of either of the methods outweigh the limitations. Both methods are accurate and can be performed simply and more universally than existing methods.

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Spectrophotometric Procedure for Quantitative Estimation of Vitamins D

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A modified antimony trichloride reagent using ethylene chloride as a solvent is suggested for the estimation of vitamin D. This modified reagent is readily reproducible, is stable over several weeks, and reacts with the vitamin to give a salmon-pink solution exhibiting an absorption maximum at 500 mμ. The reagent has been applied to the estimation of vitamin D in a variety of materials. A simple chromatographic procedure suggested for the separation of vitamin D from vitamin A and sterols utilizes a weak source of ultraviolet rays to permit observation of the materials on the column. The results of the chemical procedure are in good agreement with those obtained by biological assays.

A NUMBER of independent physicochemical procedures have been proposed for the determination of the vitamin D content of fish liver oils and other vitamin preparations. Some of these procedures have given good results with highly purified samples of vitamins D_2 and D_3, but their successful application to the assay of common fish liver oils has been limited.

Among the purely physical procedures is that of Reerink and van Wijk (*13*), in which the concentration of vitamin D in a solution of irradiated ergosterol is determined by measuring the optical density at the absorption maximum of 265 mμ. Töpelmann and Schuhknecht (*18*), Fuchs and Beck (*6*), and Ol Khin (*12*) made use of this procedure, and Marcussen (*9*) applied the technique to a few fish liver oils.

Various colorimetric methods have received more extensive study and application. Shear (*16*) suggested a colorimetric method based upon the reaction between vitamins D and an aniline–hydrochloric acid reagent. Stoeltzner (*17*) treated the vitamin with phosphorus pentachloride, but Christensen (*3*) showed that this reaction was not specific for vitamin D. Cruz-Coke (*4*) based a test on the development of a green color when an alcoholic solution of irradiated ergosterol was treated with hydrochloric acid. Meesemaecker (*10*) showed that irradiated ergosterol gave a yellow-green solution when treated with a modified Liebermann reagent. Robinson (*15*) suggested a colorimetric method based on the yellow color formed when an alcoholic solution of vitamin D was boiled with sodium nitrite and acetic acid.

A more quantitative method was proposed in 1936 by Halden and Tzoni (*7, 8, 19*), who showed that a deep violet color is obtained when an alcoholic solution of vitamin D is treated with anhydrous aluminum chloride in the presence of pyrogallol. Cholesterol and ergosterol do not interfere with the test, but vitamin A and the carotenoids must be quantitatively removed. The authors report that the method is sensitive to 2 micrograms of the pure vitamin.

Perhaps the most widely employed test is that employing a solution of antimony trichloride in chloroform, which was proposed by Brockmann and Chen (*2*) in 1936. Brockmann (*1*) used this method in his work on the isolation and identification of vitamin D from tuna liver oil, but it is applicable only to concentrated solutions of vitamin D which are relatively free from inactive sterols, vitamin A, and the inactive irradiation products from ergosterol. Wolff (*22*) asserted that the error of the procedure is ±19%, and Ritsert (*14*) reported that the method was inapplicable to fish liver oils or to mixed irradiation products from the sterols.

Nield, Russell, and Zimmerli (*11*) modified the Brockmann-Chen reagent by adding a small amount of acetyl chloride, and obtained a marked increase in stability, reproducibility, and sensitivity of reaction. Ewing, Kingsley, Brown, and Emmett (*5*) applied this modified reagent to the assay of fish liver oils, using a chromatographic procedure to remove interfering sterols and vitamin A.

This review indicates the nature of the obstacles to be overcome in the application of physical or chemical methods to the determination of vitamin D. Vitamin A, sterols, and carotenoids interfere with the direct spectrophotometric and colorimetric methods, and must be removed quantitatively. Some of the proposed reagents lack specificity and sensitivity, and are difficult to prepare or to reproduce. In many cases, the reaction between vitamin D and the reagent gives a fleeting color, and the determination must be completed within a few seconds after the solutions are mixed.

In order to overcome some of these difficulties, the authors have employed a simple chromatographic technique for separation of the vitamin from interfering substances, and have devised a modified antimony trichloride reagent which offers increased ease of preparation, increased reproducibility, and greater sensitivity and produces a more permanent color with vitamin D. The procedure has been applied to the assay of a number of fish liver oils, irradiated materials, and multivitamin preparations. Most of the results have been checked by biological assays.

EXPERIMENTAL

Preparation of Reagent. Care must be taken to ensure that all materials are free from moisture. Twenty grams of reagent grade antimony trichloride are mixed with approximately 10 grams of anhydrous calcium chloride, and pulverized in a mortar. The powdered material is shaken with 100 ml. of ethylene chloride (boiling point 83–84° C.) and filtered rapidly through anhydrous sodium sulfate. Two milliliters of acetyl chloride (boiling point 49–52°) are added to each 100 ml. of filtrate. This reagent is ready for use after 30 minutes, and is stable over a period of at least 10 weeks.

Table I. Extinction Coefficients of Products of Reaction with Vitamin D

(Each reagent contained 20 grams of $SbCl_3$ per 100 ml. of solvent and 2 ml. of acetyl chloride per 100 ml. of reagent)

Reagent No.	Solvent	Extinction Coefficient	Remarks
1	Chloroform	1800	Nield's reagent
2	Methylene chloride	2070	Reagent unstable
3	Ethylene chloride	2200	....
4	Propylene chloride	2100	Less stable than 3
5	Carbon tetrachloride	...	No reaction
6	Monochlorobenzene	1400	....

Table II. Relationship between Absorption at 500 mμ and Vitamin Concentration

Vitamin Concentration γ/10 ml.	Density
5	0.15
10	0.26
15	0.35
20	0.445
25	0.56
30	0.65
35	0.74
40	0.85
50	1.05

Preparation of Adsorption Column. An Allihn sugar tube, 2 × 10 cm., fitted with a fritted filter of medium porosity may be used for the preparation of the adsorption column. The tube is fitted to a suitable suction flask, vacuum is applied, and small portions of a 1 to 1 mixture of magnesia (Baker's Reagent Grade is suitable) and diatomaceous earth (Celite) are packed firmly until a column approximately 6 cm. in length is obtained. A 1-cm. layer of anhydrous sodium sulfate is placed on the top of the column, and packed tightly.

Saponification and Extraction. A quantity of fish liver oil sufficient to yield approximately 25 micrograms or more of the vitamin is boiled 30 minutes with freshly prepared 12% alcoholic potassium hydroxide, maintaining a ratio of 2.5 grams of potassium hydroxide per gram of oil. The alcohol volume is maintained constant throughout. At the end of the saponification period, the mixture is cooled, diluted with an equal volume of distilled water, and extracted 10 times with 50-ml. portions of anesthesia grade ethyl ether. (In case the sample weighs 10 grams or more, the extraction technique may be modified as follows: After addition of the water, add 25 ml. of ethyl acetate and 50 ml. of petroleum ether, and shake 30 seconds. Allow to stand 2 minutes, transfer the aqueous layer to another separatory funnel, and extract 10 times with a mixture of 10% ethyl ether and 90% petroleum ether. Combine extracts and continue as above.)

The extracts are combined and washed with distilled water until the washings are neutral to phenolphthalein. The extracts are dried by filtration through anhydrous sodium sulfate, the ethyl ether is removed by evaporation, and the residue is dissolved in a minimal volume of petroleum ether for chromatographing.

In the case of capsules, either vitamin D or multivitamin preparations, 5 or more capsules may be opened, and the oily contents quantitatively removed by repeated washing with ethyl ether. The ether is removed by evaporation, and the oily residue saponified as above. In an alternative procedure, which has proved successful with solid-type gelatin capsules, the capsules are boiled with the alcoholic potassium hydroxide exactly as in the case of the oils.

Tablets and other solid materials are pulverized in a mortar, and the entire mass is boiled with alcoholic potassium hydroxide for 30 minutes. The solids are removed by centrifugation, reheated with fresh portions of alcoholic potassium hydroxide, and again centrifuged. The liquids are combined and extracted with ethyl ether as in the case of the oils. The solid portion is transferred to a Büchner funnel and repeatedly extracted with ethyl ether, and the extracts are combined with those from the liquid portions.

Chromatographic Technique. The column is wetted with 50 ml. of petroleum ether, the ethereal portion from the saponification procedure is added, and the chromatogram is developed with 5-ml. portions of petroleum ether. The procedure is observed under ultraviolet rays of low intensity from a lamp described by Wilkie and De Witt (*21*). Several distinct zones of fluorescence may be observed, starting from the top of the column:

1. A narrow band of intense pale blue fluorescence.
2. A broad band of greenish-yellow fluorescence which contains vitamin A.
3. A narrow band of light gray fluorescence.
4. Two narrow bands approximately 2 mm. apart showing a bluish fluorescence.
5. A narrow band of gray-blue fluorescence ("sterol fraction").

Continued washing of the column with petroleum ether elutes zones 3, 4, and 5. The eluate from each zone is collected separately and evaporated on the steam bath. The residues are transferred to suitable glass-stoppered volumetric flasks, and made to volume with petroleum ether. Aliquots from each portion are examined by the spectrophotometric procedure to determine that separation of vitamin D from other materials is complete. In case of incomplete separation, a second chromatographing may be necessary.

The eluate from zone 5 contains the bulk of the inactive sterols, that from zone 4 contains vitamin D, and that from zone 3 may contain small amounts of vitamins A and D. All eluates are made to the same volume, which should be adjusted so that the portion from zone 4 contains approximately 1000 I.U. of vitamin D per milliliter.

Spectrophotometric Procedure. The petroleum ether solution (0.5 ml.) is placed in a 10-ml. glass-stoppered graduated cylinder and 9.5 ml. of the antimony trichloride reagent are added. The cylinder is shaken vigorously, the solution transferred to the absorption cell, and the $E^{1\%}_{1\,cm.}$ at 500 mμ determined on the Beckman spectrophotometer. Readings are made at the end of 30 seconds, and at 1-minute intervals for the first 5 minutes after starting to add the reagent to the vitamin sample. Under these conditions, sterols react slowly to give a low initial optical density which increases very rapidly to reach a maximum after approximately 5 minutes. Vitamin D reacts rapidly, giving a maximum optical density within 1 minute, and remaining constant for 5 to 10 minutes.

The potency of the vitamin preparation is obtained by multiplying the $E^{1\%}_{1\,cm.}$ of the solution by the factor of 18,200, obtained by repeated checks of the reagent against crystalline vitamins D_2 and D_3.

DISCUSSION OF PROCEDURE AND RESULTS

The preliminary experiments in this study dealt with the reagents that had been proposed, and with possible modifications designed to increase the accuracy or ease of determination. The reagent proposed by Nield, Russell, and Zimmerli (*11*) was found relatively satisfactory, but it possessed several objectionable features. The chloroform used as the solvent had to be freed of all traces of alcohol and moisture, and the purified solvent was unstable. The reagent was hygroscopic, and showed an increased sensitivity toward sterols if allowed to stand several weeks.

Further experiments were designed to study the effects of changes in the concentration and identity of each of the three components of the reagent. It was found that the concentration of antimony trichloride and of acetyl chloride could be varied over wide limits without producing significant changes in the sensitivity of the reagent, and that the substitution of mono-, di-, and trichloroacetyl chlorides for acetyl chloride produced little change. However, a marked change in the reaction was produced when chloroform was replaced by other halogenated solvents, as is shown in Table I. The use of methylene chloride, ethylene chloride, or propylene chloride gave a reagent of increased sensitivity, as is shown by the increase in $E^{1\%}_{1\,cm.}$ values. However, the methylene chloride reagent was unstable, and decomposed within a few hours after preparation. The reagent prepared from ethylene chloride was slightly more sensitive and was stable over a period of at least 10 weeks. The salmon-pink color of the solution resulting from the reaction of this reagent with vitamins D_2 and D_3 shows maximum absorption within 30 seconds, and remains stable for several minutes. The solution exhibits a narrow absorption band with maximum absorption at 500 mμ, and absorbs none of the incident light at 550 mμ. As

shown in Table II, the amount of absorption is proportional to the concentration of vitamin D, and concentrations of the vitamin as low as 5 micrograms per 10 ml. of solution may be measured under the experimental conditions.

This initial phase of the work involved studies of the reaction between crystalline vitamins D_2 and D_3 and the reagent. The second phase involved the application of the reagent to the estimation of vitamin D in a variety of materials. Crystalline vitamins D_2 and D_3 were used as standards of reference in this study. The results of the spectrophotometric determination were checked by biological assays.

The chromatographic technique is unique in that it employs a simple procedure permitting rapid separation of vitamin D from interfering sterols and vitamin A. The use of the weak source of ultraviolet light permits close observation of the column, and enables the analyst to locate the different substances with greater ease and accuracy than is possible by the use of dyes as in the method of Brockmann (*1*).

The experimental results obtained by the application of the method to a limited number of samples are given in Table III, and are self-explanatory. In general, the results are in good agreement with those obtained by biological assay. Differences, where they occur, may be due to several causes, including the errors inherent in all biological assays. Another possible cause of discrepancy arises from the fact that the bioassays were designed to show that the potency of the material was approximately equal to or greater than the given figure, and would not permit close estimation of the exact potency.

The limitations of the method have not been fully determined. With high-potency materials such as those listed in the first part of Table III, the spectrophotometric procedure has shown a high degree of accuracy and reproducibility.

Several commercial samples were examined by the spectrophotometric procedure, and were then assayed biologically in the laboratories of the U. S. Food and Drug Administration. Portions of these samples were resubmitted for spectrophotometric examination at a later date without knowledge that they had been previously analyzed. The results obtained in the second examination were within ±2% of the previous values.

A further check of the procedure involved the assay of a series of oils prepared by J. Waddell of E. I. du Pont de Nemours & Co. The samples were submitted as unknowns, with no declaration of potency. The results of this study are given in Table IV, in which the spectrophotometric values are compared with the potencies assigned by Waddell after biological assays in three independent laboratories. The biological values are expressed in terms of A.O.A.C. units, while the spectrophotometric values are in terms of micrograms. Since Waddell (*20*) reports that crystalline vitamin D_3 contains 49,222,000 A.O.A.C. units per gram, the agreement between the spectrophotometric and biological values is fairly close.

Although the values shown in part B of Table III indicate that it is possible to obtain satisfactory results in the spectrophotometric examination of low-potency oils, it is felt that the question of the applicability of the procedure to such materials has not been fully determined. The reproducibility of results in duplicate assays is less satisfactory than in the case of high-potency materials, and some modifications or refinements of procedure may be necessary in order to obtain uniformly satisfactory results.

Table III. Results of Spectrophotometric and Biological Assays of Vitamin D Carriers

Sample No.	Vitamin D Content: Bioassay	Vitamin D Content: Spectrophotometric	Remarks
	U.S.P. units per gram		
	A. Vitamins D_2 and D_3 in Oil		
72442	200,000	198,000	D_3 in corn oil. A.O.A.C. assay
12313	400,000	422,000	Irradiated ergosterol
12314	400,000	389,000	Irradiated ergosterol
34074	10,000	8,950	D_3 in sesame oil
73142	166,500	165,000	D_3 in corn oil
B 72144	200,000	198,300	No bioassay, figure from label declaration
	U.S.P. units per capsule		
74290	50,000	57,300	D_3 in capsules
60910	50,000	48,900	Capsules
VA 9108	50,000	52,650	Capsules, with semisolid gelatin medium
60932	50,000	54,550	Solid-type gelatin capsules
59801	50,000	53,000	No bioassay, figure from label
58347	50,000	57,950	No bioassay, figure from label
VA 5573	40,000 approx.	42,800	Label declares 50,000 per capsule
51408	50,000	47,800	
	B. Vitamins A and D in Oil		
	U.S.P. units per gram		
92244	115	113	
23606	400	395	
12073	....	160	More than 85 U.S.P. units per gram by bioassay
23607	400	410	
72144	10,000	10,385	50,000 A per gram
61544	....	42	Less than 50 units per gram by bioassay
	U.S.P. units per capsule		
11143	1,000	1,040	5000 A per capsule
2243	1,000	1,020	5000 A per capsule
41543	1,000	1,050	5000 A per capsule
	U.S.P. units per gram		
VA 7048	10,000	11,250	50,000 A per gram
10143	10,000	9,725	50,000 A per gram
	U.S.P. units per capsule		
1144	1,000	950	5000 A per capsule
	C. Multivitamin Preparations		
92044	1,000	1,050	6 vitamin capsules
91944	200	205	Hexavitamin capsules
	U.S.P. units per tablet		
C 1234	200	220	Hexavitamin tablets

Table IV. Results of Spectrophotometric and Biological Assays of Vitamin D Carriers

Sample No.	Vitamin D Content: Bioassay *A.O.A.C. units/g.*	Vitamin D Content: Spectrophotometric *γ/g.*	Spectrophotometric *A.O.A.C. units/g.*[a]
1	1,000,000	20,125	986,000
2	500,000	10,100	494,000
3	1,150,000	22,300	1,092,700
4	575,000	10,800	529,000

[a] Calculated on basis that 1 gram of crystalline D_3 contains 49,200,000 A.O.A.C. units.

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The data in this paper are taken in part from a thesis submitted by James B. De Witt in partial fulfillment of the requirements for the degree of doctor of philosophy, Georgetown University, 1944.

Precipitation of Platinum Metals by Organic Monosulfides

Determination of Platinum with Thiophenol and Rhodium with Thiobarbituric Acid

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This report deals with a preliminary investigation of organic monosulfide compounds as analytical reagents for the platinum metals. The action of seven organic monosulfide compounds with some of the platinum and related metals is described. It has been found that rhodium may be determined gravimetrically with thiobarbituric acid. Thiophenol may be used as a precipitant in the gravimetric determination of platinum.

THE reactions of organic sulfide compounds with many metals have been studied extensively. Zeise (*14*) in 1834 chose the name "mercaptan" for C_2H_6SH because of the reaction of this compound with mercury. He also described (*15*) its reaction with platinum. Many references have been made in the literature to further researches on organic sulfide compounds with platinum metals, most of them concerned with the study of the methods of preparation and stereoisomerism of the various compounds produced. Some of these reactions have formed the basis for analytical procedures for platinum metals. Berg and coworkers (*4–8*) investigated the action of thionalide (thioglycollic-β-aminonaphthalide) with many metals, and Kienitz and Rombock (*10*) used it for the volumetric estimation of rhodium. Rogers, Beamish, and Russell (*12*) determined ruthenium gravimetrically by precipitation with thionalide.

The reactions of organic monosulfide compounds with platinum metals have been examined with a view to finding useful analytical methods for their determination and relating the configuration of the organic compounds with their ability to precipitate these metals. The precipitation of several platinum and associated metals under various conditions of acidity with seven organic monosulfide compounds has been investigated. In some cases the precipitation of various platinum metals is complete. Rhodium may be determined gravimetrically with thiobarbituric acid. Thiophenol may be used as a precipitant in the determination of platinum.

PRECIPITATION REACTIONS

Standard solutions of platinum, palladium, rhodium, iridium, gold, nickel, copper, and iron containing approximately 1 mg. of metal per ml. of solution were prepared by dissolving the pure metal or a suitable pure salt in aqua regia, hydrochloric acid, or water, removing the nitric acid, if present, by fourfold evaporation to dryness in the presence of hydrochloric acid, and finally dissolving in a solution containing 1 ml. of concentrated hydrochloric acid per liter.

A 10-ml. aliquot of the standard metal solution under investigation was diluted and acidified to one of the six acid conditions given in Table I. The organic reagent was added and the solution heated and maintained at boiling for 2 hours. The total volume of the solution was maintained at 200 ml. by additions

Table I. Precipitation of Platinum Metals

N. No precipitation, or precipitate contained none of metal under investigation
S. Very slight precipitation
P. Partial precipitation
C. Complete precipitation; filtrate contained less than 0.02 mg. of metal under investigation

Reagent	Amount of Reagent	Metal, 10 Mg.	Acid Strength: 1:3 aqua regia 0.012 *N*	HCl 0.012 *N*	HNO_3 0.012 *N*	1:3 aqua regia 0.60 *N*	HCl 0.60 *N*	HNO_3 0.60 *N*
Allyl thiourea	1 ml. of 2% w/v soln. in 95% ethanol	Pt	N	N	N	N	N	P
		Pd	P	C	C	N	P	P
		Rh	N	N	N	N	P	P
		Ir	N	N	N	N	N	N
		Au	P	C	P	N	C	C
		Ni	N	N	N	N	N	N
		Cu	N	N	N	N	N	N
		Fe	N	N	N	N	N	N
Phenyl thiourea	1 ml. of 3% w/v soln. in 95% ethanol	Pt	P	P	P	N	P	P
		Pd	C	C	C	P	P	P
		Rh	P	P	P	N	P	S
		Ir	S	N	S	N	P	N
		Au	P	C	P	N	P	P
		Ni	N	N	N	N	N	N
		Cu	S	S	S	N	S	N
		Fe	N	N	N	N	N	N
s-Di-*o*-tolyl thiourea	10 ml. of 0.8% w/v soln. in 95% ethanol	Pt	P	P	P	P[a]	C	P
		Pd	P	P	C	P	C	C
		Rh	P	P	P	P	P	P
		Ir	N	N	N	N	N	N
		Au	P	P	P	P	C	P
		Ni	N	N	N	N	N	N
		Cu	P	P	P	P	P	P
		Fe	N	N	N	N	N	N
Thiophenol	1 ml. of 4% v/v soln. in 95% ethanol	Pt	P	C	C	P	P	P
		Pd	C	C	C	P	C	C
		Rh	P	P	P	P	P	P
		Ir	P	P	P	P	P	P
		Au	C	C	C	N	C	C
		Ni	N	N	N	N	N	N
		Cu	P	P	P	N	S	P
		Fe	N[b]	N[b]	N[b]	N	N[b]	N
Phenyl thiohydantoic acid	2 ml. of 2.1% w/v soln. in 95% ethanol	Pt	P	P	P[a]	N	P	P
		Pd	P	P	C[c]	P	P	C[c]
		Rh	P	P[a]	P	P	P	P
		Ir	S	S	S	N	N	N
		Au	C	P	C	N	C	C
		Ni	N	N	N	N	N	N
		Cu	P	P	P	P	P	P
		Fe	N	N	N	N	N	N
Thiobarbituric acid	2.5 ml. of 1.4% w/v soln. in 95% ethanol	Pt	C	C	C	C	C	P
		Pd	C	C	C	C	C	P
		Rh	P	C	C	P	P	P
		Ir	P	P	P	P	P	N
		Au	C	C	C	P	C	N
		Ni	N	N	N	N	N	N
		Cu	S	S	S	N	N	N
		Fe	N	N	N	N	N	N
s-Diphenyl thiourea	5 ml. of 1% w/v soln. in 95% ethanol	Pt	P	P	P	P	P	P
		Pd	C	C	C	P	C	P
		Rh	P	P	P	S	P	S
		Ir	S	S	S	N	S	N
		Au	C	C	P	S	P	S
		Ni	N	N	N	N	N	N
		Cu	N	N	N	N	N	N
		Fe	N	N	N	N	N	N

[a] Nearly complete.
[b] Slight precipitate containing possibly a little iron.
[c] Not boiled.

of water when necessary. If a precipitate formed, the mixture was filtered and the filtrate tested for the metal.

The organic reagents are listed in Table I, with results for the metals investigated. The solid compounds were purified by crystallization from ethanol.

The spot tests used for platinum, palladium, iridium, and rhodium were discussed by Thompson, Beamish, and Scott (*13*). Stannous chloride was used for platinum, palladium, rhodium and gold, sulfuric and fuming nitric acids for iridium, dimethyl glyoxime for nickel, and ferrocyanide for iron and copper.

In many cases where complete precipitation was obtained gravimetric determinations for the metals were carried out. The precipitate and filter were ignited, reduced by burning in hydrogen if necessary, cooled in nitrogen if reduced, or in air, and weighed as the metal.

Some of the results for these determinations are listed in Table II. A number of the results were slightly high (typified by Nos. 1 to 3).

Phenyl thiourea, thiophenol, and thiobarbituric acid are suitable for the determination of palladium. Mann and Purdie (*11*) stated that thiophenol precipitated a $Pd(SPh)_2$ which decomposes to palladium quantitatively when heated, but they did not outline a method for its determination or record results. The results obtained for the determination of gold by thiophenol tend to be slightly high.

The platinum solution for determinations 1 to 3 was standardized by the thiophenol method, by the sodium formate method (*3*), and by precipitation with zinc (*2*). The palladium solutions were standardized by the potassium iodide method (*1*) and the gold solutions by the hydroquinone method (*3*).

Table II. Determination of Metals

Detn. No.	Reagent	Acid	Normality of Acid	Metal Determined	Metal Taken, Mg.	Metal Recovered, Mg.
1	s-Di-o-tolyl thiourea	HCl	0.60	Platinum	19.18	19.49
2	s-Di-o-tolyl thiourea	HCl	0.60	Platinum	19.18	19.51
3	s-Di-o-tolyl thiourea	HCl	0.60	Platinum	19.18	19.54
4	Phenyl thiourea	Aqua regia	0.012	Palladium	10.00	10.00
5	Phenyl thiourea	HCl	0.012	Palladium	10.00	10.00
6	Phenyl thiourea	HNO_3	0.012	Palladium	10.00	10.02
7	Phenyl thiohydantoic acid	HNO_3	0.60	Palladium	10.00	10.03
8	Thiophenol	HCl	0.012	Palladium	9.91	9.97
9	Thiophenol	HCl	0.012	Palladium	24.98	24.96
10	Thiophenol	HCl	0.012	Palladium	24.98	25.00
11	Thiophenol	HCl	0.012	Palladium	24.98	24.98
12	Thiophenol	HCl	0.012	Palladium	24.98	24.96
13	Thiophenol	HCl	0.012	Palladium	24.98	25.00
14	Thiophenol	HCl	0.012	Palladium	24.98	24.98
15	Thiobarbituric acid	HCl	0.012	Palladium	9.82	9.86
16	Thiobarbituric acid	HCl	0.06	Palladium	9.82	9.82
17	Thiobarbituric acid	HCl	0.06	Palladium	9.82	9.86
18	Thiobarbituric acid	HCl	0.30	Palladium	9.82	9.83
19	Thiobarbituric acid	HCl	0.30	Palladium	9.82	9.84
20	Thiophenol	Aqua regia	0.012	Gold	10.56	10.68
21	Thiophenol	HNO_3	0.012	Gold	10.56	10.53
22	Thiophenol	HNO_3	0.60	Gold	10.56	10.54
23	Thiophenol	HCl	0.012	Gold	10.56	10.66
24	Thiophenol	HCl	0.012	Gold	25.26	25.34
25	Thiophenol	HCl	0.012	Gold	25.26	25.32
26	Thiophenol	HCl	0.012	Gold	25.26	25.29
27	Thiophenol	HCl	0.012	Gold	25.26	25.37
28	Thiophenol	HCl	0.012	Gold	25.26	25.34
29	Thiophenol	HCl	0.012	Blank	0.00	−0.01
30	Thiophenol	HCl	0.012	Platinum	9.97	9.97
31	Thiophenol	HCl	0.012	Platinum	9.97	9.96
32	Thiophenol	HCl	0.012	Platinum	9.97	9.97
33	Thiophenol	HCl	0.012	Platinum	9.97	9.98
34	Thiophenol	HCl	0.012	Platinum	25.13	25.12
35	Thiophenol	HCl	0.012	Platinum	25.13	25.20
36	Thiobarbituric acid	HCl	0.03	Rhodium	25.08	25.09
37	Thiobarbituric acid	HCl	0.03	Rhodium	25.08	25.12
38	Thiobarbituric acid	HCl	0.03	Rhodium	25.08	25.08
39	Thiobarbituric acid	HCl	0.03	Rhodium	25.08	25.08
40	Thiobarbituric acid	HCl	0.03	Rhodium	25.08	25.07
41	Thiobarbituric acid	HCl	0.03	Rhodium	25.08	25.10
42	Thiobarbituric acid	HCl	0.03	Rhodium	25.08	25.09
43	Thiobarbituric acid	HCl	0.012	Rhodium	25.08	25.03
44	Thiobarbituric acid	H_2SO_4	0.036	Rhodium	25.08	25.16
45	Thiobarbituric acid	HCl	0.30	Rhodium	25.08	25.13

DETERMINATION OF PLATINUM

As a result of this investigation a new method was developed for the gravimetric determination of platinum by precipitation with thiophenol.

The platinum solution was prepared from pure platinum sponge which was dissolved in aqua regia, evaporated to dryness over a steam bath four times in the presence of concentrated hydrochloric acid, and finally dissolved in very dilute hydrochloric acid, filtered through a 7-cm. Whatman No. 44 paper, and washed. The filter paper was ignited, and the residue dissolved in aqua regia, evaporated to dryness four times with hydrochloric acid, dissolved in water, and filtered. The filtrates were diluted to the required volume and acidified to 1 ml. of concentrated hydrochloric acid per liter.

An aliquot of the solution containing approximately 10 to 25 mg. of platinum was diluted to 200 ml. and acidified with 4 drops of concentrated hydrochloric acid. One milliliter of a fresh 10% by volume solution of thiophenol in 95% ethanol was added to the cold solution, which was then boiled for 2 hours, filtered through a Whatman No. 44, 7-cm. filter paper, and washed with water. The paper and residue were permitted to drain and while still moist were transferred to a Coors 000 porcelain crucible and heated, commencing with a small flame. When smoke was no longer produced at that burner setting, the flame was gradually increased and the slow ignition was continued until the paper was thoroughly charred. The residue was then ignited at red heat for 20 minutes, cooled, and weighed. High results were obtained if the residue were ignited immediately at high temperature.

In order to facilitate the slow ignition of the residues a draft-free combustion chamber was made from Transite with holes along the bottom of each side to permit entry of air. It was fitted with a thin glass cover supported about 1 cm. above the top of the cupboard and a window for easy observation of the combustion. Upon evaporation of the filtrate platinum proved to be absent. Complete precipitation was obtained with an acid strength as great as 0.05 *N*, but a greater acid strength resulted in incomplete precipitation. Results appear in Table II (30 to 35).

The reagent tends to oxidize on exposure to air and incomplete precipitation is obtained with the partially oxidized reagent. The precipitate was a characteristic yellow-green color. When the oxidized reagent was used, or the reagent was added to a hot solution, the precipitate became orange-colored on boiling. The reagent may be kept in a small vial placed inside a large Nesbitt tower. The air is swept from the tower by means of a stream of nitrogen, and the tap on the tower is closed to keep the reagent in the nitrogen atmosphere. The reagent should be freshly prepared every 3 or 4 days. Five drops of thiophenol may be used instead of 1 ml. of the 10% thiophenol reagent.

DETERMINATION OF RHODIUM

A method was developed for the gravimetric determination of rhodium by precipitation with thiobarbituric acid.

The rhodium solution was prepared by dissolving a sodium salt of rhodium chloride in water containing 0.5 ml. of hydrochloric acid, filtering, washing thoroughly, and diluting to 2 liters. (The "sodium rhodium chloride" was donated by the International Nickel Company of Canada.) The solution was standardized by the hydrogen sulfide method (*9*). An aliquot of solution containing approximately 25 mg. of rhodium was diluted to 200 ml. and acidified with 0.5 to 5 ml. of hydrochloric acid, 10 ml. of 1.4% w/v thiobarbituric acid in 95% ethanol were added, and the solution was heated to boiling. The pink solution became a dark red-brown in color. After boiling 2 to 3 minutes a very fine red-brown precipitate appeared. The solution was boiled for 2 hours and the precipitate settled out as chocolate-brown crystals. The mixture was filtered, washed, ignited at red heat for 20 minutes, reduced in hydrogen, cooled in nitrogen, and weighed. Results are included in Table II (36 to 45).

Spot tests on the evaporated filtrates proved the absence of rhodium. This method presents greater ease of operation than the hydrogen sulfide method. The results obtained by both methods agree very closely. Thiobarbituric acid is the first organic precipitant proposed for the gravimetric determination of rhodium.

An attempt was made to determine the composition of the rhodium–thiobarbituric acid complex.

A rhodium precipitation was carried out in ethanol with thiobarbituric acid reagent. The precipitate was filtered, washed with ethanol, dried under reduced pressure, and weighed. The residue was transferred to a small beaker, the organic matter destroyed with sulfuric and nitric acids, and the rhodium determined by the hydrogen sulfide method. The percentage of rhodium in the complex averaged from three determinations was 26.7%.

If two molecular weights of thiobarbituric acid were combined with one atomic weight of rhodium, the latter replacing one hydrogen of each thiobarbituric acid molecule, the amount of rhodium present would be 26.5%. If one rhodium were associated with three thiobarbituric acid molecules the amount of rhodium present would be 19.3%. The valence of 2 for rhodium corresponds to the usual valence for other metals with organic compounds of this type but is an uncommon valence for rhodium.

SUMMARY

With the organic monosulfide compounds used in this investigation, palladium and gold seem to be most readily precipitated completely under the conditions described. However, platinum forms precipitates completely in many cases. It is more difficult to precipitate rhodium and iridium. Copper, nickel, and iron do not form precipitates readily with these reagents.

Conditions are described for the gravimetric determination of rhodium by thiobarbituric acid and of platinum by thiophenol.

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Hexamethylenetetramine in Separations of Titanium and Columbium

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A procedure for gravimetric determination of titanium in ferrotitanium alloys is reported, in which hexamethylenetetramine eliminates the use of hydrogen sulfide for removal of iron. Sodium hydroxide and hexamethylenetetramine are used in a procedure for determining columbium, titanium, or both in high chromium-nickel steels containing tungsten, vanadium, and molybdenum. The procedures are believed to be applicable to determination of zirconium.

THE use of hexamethylenetetramine has been developed in the following procedures to separate divalent iron from titanium and columbium.

Lehrman (*4*, *5*) used hexamethylenetetramine qualitatively to separate divalent ions from numerous trivalent and tetravalent ions. Specific quantitative procedures using the reagent have been developed (*1*, *2*, *3*, *6*, *7*) to separate trivalent iron, aluminum, chromium, and titanium from zinc, nickel, cobalt, manganese, calcium, and magnesium.

These references indicated a method of separating iron from titanium and columbium contained in ferro-alloys or stainless steels, based on reduction of iron to the divalent state. The iron of those alloys and steels that may require an oxidizing acid for solution can be readily reduced by zinc after removal of the oxidant. Two procedures have been developed: one for the gravimetric determination of titanium in ferrotitanium alloys, the other for the determination of titanium and columbium in high chromium-nickel steels.

REAGENTS

All reagents used were the usual c.p. grade. Hexamethylenetetramine was purchased from the Eastman Kodak Company. Zinc spirals were obtained from the G. Frederick Smith Company, Columbus, Ohio.

GRAVIMETRIC DETERMINATION OF TITANIUM IN FERROTITANIUM ALLOYS

In a reduced solution hexamethylenetetramine will precipitate titanium and leave the iron in solution, presenting many advantages over the hydrogen sulfide method for the removal of iron:

1. It eliminates the use of obnoxious hydrogen sulfide and permits the operations to be performed on the working bench without any unusual ventilation.
2. The desired element, titanium, is precipitated, thus removing any possible loss by hydrolysis.
3. After a hydrogen sulfide separation the filtrate must be boiled to remove this reagent. It has been the experience of the author that the sulfur residue has always contained a trace of titanium that requires an additional operation to recover.
4. Titanium precipitated with hexamethylenetetramine will filter much faster than the bulky iron sulfide precipitate.
5. No precipitates or residue requires working in platinum. This eliminates the necessity of removing traces of platinum.

Any zirconium will be found with the titanium, and appropriate means for its determination may be taken.

Many common separations have been used to complete the desired analysis, such as cupferron and sodium hydroxide, and are mentioned only by name. Complete details can be found in any standard reference.

Procedure A. Place 0.5000 gram of 80-mesh alloy in a 400-ml. beaker, add 100 ml. of 5% sulfuric acid, and heat gently until the reaction has ceased. Add nitric acid dropwise until the sample is oxidized. Make a sodium hydroxide separation to remove vanadium. Transfer the washed precipitate and paper to the beaker in which it was made. Destroy the organic matter with 15 ml. of sulfuric acid, 25 ml. of nitric acid, 10 ml. of perchloric acid (70 to 72%), and 5 to 8 grams of sodium sulfate by covering and evaporating to fumes of sulfuric acid. Make sure that all the perchloric acid has been removed. Cool and dilute the sample to 150 ml. with water. Heat the sample until all the salts are in solution, introduce an amalgamated zinc spiral, and reduce the solution. Since all the iron will reduce before any titanium, the deep violet color of reduced titanium will indicate the complete reduction of iron to the divalent state.

Remove the spiral and add 3 to 4 drops of 10% aerosol (wetting agent obtained from any chemical supply house). By lowering the surface tension of the solution the air oxidation of divalent iron is eliminated. Add ammonium hydroxide dropwise until the black precipitate that forms just redissolves. Add a 10% solution of hexamethylenetetramine until the sample is alkaline to methyl red, introduce a little ashless paper pulp, and

Table I. Determination of Titanium

B. of S. Sample	Ti Contained %	Ti Found %
	Procedure A	
116	25.48	25.43 25.50
116A	25.08	25.09 25.05 25.08 25.11
	Procedure B	
116	25.48	25.53
116A	25.08	25.10 25.13 25.10[a] 25.14[b]

[a] Contained 0.25 gram of V.
[b] Contained 0.5 gram of V.

boil for 1 minute. Filter on a medium texture paper using a moderate suction, and wash the precipitate 5 to 6 times with a hot 0.5% hexamethylenetetramine solution.

Return the precipitate and paper to the beaker and destroy the organic matter as described above. After the perchloric acid has been removed, cool, dilute the sample to 100 ml. with water, heat to boiling, and filter. Wash the residue with hot water, and discard. (It will be silicic acid with possibly some aluminum oxide.) Heat the filtrate and reduce it with a zinc spiral. Repeat the ammonium hydroxide and hexamethylenetetramine separation.

If the sample contains copper, destroy the hexamethylenetetramine precipitate and paper as above. Dilute the sample to 200 ml. with water and make an ammonium hydroxide separation with a 5% excess. Boil, filter, and wash the precipitate with a hot 5% ammonium hydroxide solution.

Transfer the precipitate and paper to the same beaker and digest it with 30 ml. of sulfuric acid. Dilute to 100 ml. with hot water and stir until the precipitate is completely in solution. Cool the sample to 10° C. and make a cupferron separation. Place the cupferron precipitate in a tared platinum dish of 75-ml. capacity, dry, and ignite with the usual precautions to a constant weight. In umpire work correct the titanium dioxide for traces of silica and iron. Convert the corrected weight of titanium dioxide to titanium (Table I, A).

Inasmuch as vanadium can be reduced to a valence of 2 with zinc, it was decided to investigate the possibility of eliminating the sodium hydroxide separation for its removal. This was accomplished with a considerable saving of time. Iron and titanium must be reduced to a valence of 2 and 3, respectively, before vanadium will reduce to a valence of 2. If the operator finds it difficult to determine the complete reduction of the sample, Procedure A is suggested.

Procedure B. Place 0.5000 gram of the alloy in a 400-ml. beaker with 100 ml. of 10% sulfuric acid and heat until the reaction has ceased. Introduce a zinc spiral to ensure complete reduction (15 to 30 minutes). Add 3 to 4 drops of aerosol and proceed with the double hexamethylenetetramine and ammonium hydroxide separations as given in Procedure A. Precipitate the titanium with cupferron, dry, and ignite the precipitate to a constant weight (Table II, B). Vanadium was added to two Bureau of Standards No. 116A samples as indicated.

DETERMINATION OF TITANIUM AND COLUMBIUM IN HIGH CHROMIUM-NICKEL STEELS

In the usual procedure for the determination of columbium in heat-resisting steels this element is hydrolyzed in a dilute acid solution. If the steel also contains an appreciable amount of titanium this method is not very satisfactory. Titanium can be hydrolyzed, but it is a troublesome and time-consuming analysis. When, in addition, tungsten, vanadium, and molybdenum are alloyed in the steel, the determination of columbium and titanium is further complicated.

In the author's method tungsten, vanadium, and molybdenum are removed by a sodium hydroxide separation. While it is true that columbium alone is only partially precipitated by sodium hydroxide, the results indicate that in the presence of titanium and iron, columbium can be successfully separated from tungsten and vanadium. It appears that columbium like titanium requires the presence of iron to ensure complete precipitation in a sodium hydroxide separation. It is very important that the sodium hydroxide precipitate be washed with a 2% sodium hydroxide solution. Washing the precipitate with hot water causes a loss of columbium. Molybdenum is one of the elements with a valence higher than 2 that is not precipitated by hexamethylenetetramine. If the steel contains no tungsten or vanadium but only molybdenum, no sodium hydroxide separation is necessary for its removal. Two hexamethylenetetramine separations removed the molybdenum completely from an alloy of molybdenum and titanium containing over 50% molybdenum.

If the sample contains tantalum it will be found with the columbium and titanium, and appropriate means for its determination must be taken. The developed procedure will give columbium, titanium, or both if they are present in the sample.

Procedure. Place 5.000 grams of drillings in 400-ml. beaker, add 100 ml. of 1 to 2 hydrochloric acid, and heat until the reaction has ceased. Cool the sample to 10° C. and precipitate the columbium and titanium by the usual cupferron method for titanium in steels. Be sure to precipitate sufficient iron so that columbium and titanium will not be lost in the subsequent sodium hydroxide separation (25 ml. of a 6% solution should be more than sufficient). Return the precipitate and paper to the beaker. Destroy the organic matter with 10 ml. of sulfuric acid, 25 ml. of nitric acid, 10 ml. of perchloric acid, and 3 grams of sodium sulfate, by covering and evaporating to fumes of sulfuric acid. Cool, dilute the solution with water, and make a sodium hydroxide separation to remove the tungsten and vanadium. (If no tungsten or vanadium is present omit this separation.) Wash the precipitate moderately with a hot 2% sodium hydroxide solution.

Transfer the precipitate and paper to the same beaker and destroy the organic matter as in the cupferron precipitate, making sure that all the perchloric acid is removed. Cool, dilute the sample to 150 ml. with water, add 5 ml. of hydrochloric acid, and heat. Reduce the iron with a zinc spiral (indicated by the disappearance of the yellow color due to ferric chloride). Add 3 to 4 drops of aerosol and ammonium hydroxide dropwise until the solution is nearly neutral to methyl red. The appearance of a white precipitate will be due to titanium or columbium hydroxide and is of no consequence to the removal of the iron. Add 10% hexamethylenetetramine solution until the sample is alkaline to methyl red. Introduce some ashless paper pulp and boil the sample for 1 minute. Filter and wash the precipitate 5 times with a hot 0.5% hexamethylenetetramine solution. Destroy the organic matter in the precipitate and paper as given for the cupferron precipitate. Repeat the ammonium hydroxide and hexamethylenetetramine separation.

Table II. Determination of Titanium and Columbium

B. of S. Sample	% Contained	% Found
121	0.394 Ti	0.403 Ti[a] 0.400 Ti[a]
123A	0.75 Cb	0.78 Cb[b] 0.78 Cb[b]
		0.356 Ti 0.77 Cb[b]
121A, 2.5 grams 123A, 2.5 grams	0.361 Ti 0.75 Cb	0.352 Ti 0.78 Cb[b]
		0.354 Ti 0.77 Cb[b]

[a] Weighed as TiO_2.
[b] Not corrected for Ta. Sample contains 0.02% Ta.

Transfer the precipitate and paper to the same beaker and digest it with 30 ml. of 1 to 1 sulfuric acid. Dilute the sample to 100 ml. with hot water and stir well. Cool the solution to 10° C. and make a cupferron separation. Dry and ignite the precipitate in a tared platinum dish of 75-ml. capacity. Remove silica in the usual manner with sulfuric and hydrofluoric acids.

The residue is composed of the mixed oxides of columbium and titanium. Fuse the residue with sodium bisulfate. Dissolve and determine the titanium colorimetrically with hydrogen peroxide in a 5% sulfuric acid solution. Subtract the weight of titanium dioxide from the total weight of the oxides. Convert the difference, columbium pentoxide, to columbium (Table II).

DISCUSSION

When checked by spectrographic methods the precipitates showed no mercury or zinc, indicating that there is no contamination from the amalgamated zinc spirals.

In the gravimetric determination of titanium in ferrotitanium alloys, a procedure has been developed using hexamethylenetetramine that eliminates the use of obnoxious hydrogen sulfide for the removal of the iron.

In the determination of columbium and titanium, sodium hydroxide and hexamethylenetetramine are used to determine columbium, titanium, or both in high chromium-nickel steels containing tungsten, vanadium, and molybdenum.

Preliminary investigation on synthetic mixtures of iron and zirconium indicates that the procedures are applicable to the determination of zirconium.

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Determination of Metallic Copper in Cuprous Oxide-Cupric Oxide Mixtures

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For the determination of metallic copper in cuprous oxide–cupric oxide mixtures, the cuprous oxide is dissolved in a dilute alcoholic hydrochloric acid solution and the metallic copper is determined in the insoluble metallic copper–cupric oxide residue by direct solution in acid ferric chloride followed by titration with ceric sulfate. Reaction between cupric ions and metallic copper is prevented by addition of stannous chloride which reduces the cupric ion to cuprous ion. Difficulties in the analysis of commercial copper and cuprous oxide pigments, due to physical characteristics of the pigments, are presented. The effects of exposure time, temperature, atmosphere, and solvents are listed.

A large number of analyses were made by this method on synthetic mixtures and commercial copper and cuprous oxides with excellent results. The method is rapid and accurate and requires only the apparatus found in the average laboratory. The personal factor involved in most attempts to develop a method of analysis is eliminated and only a few and relatively simple precautions are required in the performance of the analysis.

COMMERCIAL cuprous oxide and copper pigments for use in antifouling paints or insecticides are prepared by several methods. The electrolytic method for the preparation of cuprous oxide is based on the anodic oxidation of copper in an alkaline solution. By control of the current density and the temperature of the alkaline salt solution, the particle size of the cuprous oxide can be controlled to produce a cuprous oxide of high purity. Pyrometallurgical cuprous oxide is prepared by the reduction of mixed copper oxides obtained (*a*) as a by-product of wire drawing or copper annealing operations, (*b*) from the copper recovery of ore tailings, (*c*) by leaching scrap copper and rich ore concentrates, and (*d*) from cement copper powder. The mixed copper oxides are reduced by heating in a reducing atmosphere to change the cupric oxide to cuprous oxide and grinding to a controlled fineness. The cuprous oxides are then coated with a material such as stearic acid, protein, pine oil, or mineral oil to prevent oxidation on storage. A new type of copper pigment for use as a substitute for cuprous oxide in antifouling paints is prepared from cement copper, which is obtained as a sludge from acid copper mine water which has been passed over iron. The copper is displaced from solution by the iron, forming a spongy precipitate of copper particles. Each particle of copper is coated with a layer of cuprous oxide.

The particle sizes of the constituents of the copper and cuprous oxide pigments are in general nonuniform and vary from 0.2 to 30 microns with a mean average diameter ranging from 1 to 5 microns. The pigment obtained from these manufacturing operations contains various percentages of cupric oxide and metallic copper, depending on the processing received and the raw material used. Besides variations in composition, the various manufacturing processes result in different particle shapes and surface structure. In some types the cuprous oxide particles are covered with finer particles of cupric oxide. By electron microscopic photographs, the particles of cupric oxide formed in the pigment on aging or as a result of incomplete reduction in manufacture were found to be approximately one tenth the size of the cuprous oxide particles in the pyrochemical type cuprous oxide. In the copper pigments, the metallic copper contains cuprous oxide on the surface of the copper. The electrolytic pigments have particles of definite structure, whereas the pyrometallurgical pigments have irregular shaped particles. The data presented in Table I indicate the wide variation in physical properties of these pigments.

LITERATURE REVIEW

In a previous paper (*1*) the authors reviewed the difficulties involved and the results of numerous attempts to develop a quantitative determination of the components of the finely divided mixtures of cuprous oxide, cupric oxide, and metallic copper. A method was developed that gave reproducible results on a number of types of electrolytic and pyrometallurgical cuprous oxide pigments. The procedure is based on the use of a dilute aqueous hydrochloric acid solution, using hydrazine sulfate to reduce any dissolved cupric ions. Although an improvement over previous methods, further experiments have shown the method to lack sufficient accuracy. Since the publication of this paper, a number of manufacturers have undertaken the manufacture of cuprous oxide and copper pigments. Samples received from several manufacturers were analyzed, using the hydro-

Table I. Physical Properties of Cuprous Oxide and Copper Pigments

Grade	Electrolytic Cu_2O	Copper Pigment	Pyrometallurgical Cu_2O Manufacturer 1	Pyrometallurgical Cu_2O Manufacturer 2
Apparent density, lb./cu. ft.	51.2	97.8	128.8	105–132
Oil absorption, lb. of oil/100 lb. of pigment	11.7	15.2	8.1	6.5–7.1
Specific gravity	5.59		5.72	5.84–5.94
Color (Munsell)	R 4/6	R 3/6	R 4/6	R 3/4–R 4/6
Crystal structure	Star shaped	Porous	Irregular	Irregular
Average particle diameter, microns	2.1	2.5	2.1	3.0–5.0
% particles less than 1 μ	11	33	60	15–22
% particles 1–3 μ	56	46	32	19–40
% particles 3–5 μ	25	17	6	10–23
% particles over 5 μ	8	4	2	21–49

chloric acid–hydrazine sulfate method (*1*) for metallic copper content.

Negative figures are obtained for cupric oxide and two of the samples show over 100% of cuprous oxide plus metallic copper. It is believed that this is indicative of: high total reducing power, presence of other metals or reducing agents having a reducing action on ceric sulfate, or low metallic copper.

Previous results (*1*) on the determination of total reducing power using ceric sulfate showed the accuracy of this method to be satisfactory. Examination of the pigments showed that no other metals or organic matter are present in sufficient quantity to affect the results materially. Therefore, the indication is that the metallic copper is low.

DEVELOPMENT OF METHOD

One of the chief difficulties involved in developing an analytical procedure for the determination of copper in the presence of cuprous oxide and cupric oxide is in the preparation of a standard reference sample, the composition of which is definitely known. A standard prepared by mixture of a pure electrolytic cuprous oxide, copper powder, and cupric oxide is not representative of the commercial pigments. The cupric oxide in the synthetic mixtures has larger particle size and different surface structure, and is less reactive than the cupric oxide in the pigment which is often formed directly on the copper or cuprous oxide particles. The commercially prepared pigment is an intimately mixed combination of the copper cuprous oxide, and cupric oxide prepared simultaneously in situ during the manufacturing process, whereas the synthetic mixtures are composed of three definite, separate particles of copper, cuprous oxide, and cupric oxide. Moreover, the physical properties of various grades of commercial pigments are sufficiently different to alter their reactivities toward various chemical reagents. Therefore, a procedure for the determination of copper must be accurate not only for synthetic mixtures but also for all types of commercial pigments before being acceptable. Negative figures for cupric oxide and total concentrations of ingredients adding to more than 100% will aid in determining the accuracy of a procedure. Reproducibility of results cannot be used as a criterion of accuracy, but only as a determination of the personal factor involved in the method.

As previously noted, the difficulty in selectively dissolving cuprous oxide and separating it from metallic copper in the presence of cupric oxide is based on the sensitivity of the finely divided components to chemical solutions and the effect of dissolved cupric ion on metallic copper. In the previous methods, the reagents used for dissolving cuprous oxide also attacked the copper, attacked the cupric oxide without reducing the resultant cupric ions rapidly enough to prevent attack on copper, or formed reaction products that attacked the copper.

An indication of the effect of the reagent on the copper can be obtained by noting the effect of the time of contact between the reagents and the sample on the percentage of copper determined. In all previous methods, the time factor is of considerable importance, indicating that the metallic copper determinations are low. Maximum indication of accuracy is inferred from a procedure having a negligible time factor.

A reagent to be suitable must have no effect on metallic copper and slight attack on cupric oxide and must completely dissolve the cuprous oxide. A reagent that has no effect on cupric oxide is unsuitable for the determination of metallic copper in certain pyrometallurgical grade cuprous oxides, since a large portion of the cuprous oxide particles are covered with cupric oxide, thus preventing the required dissolving action. Too great an attack on the cupric oxide results in an excess concentration of cupric ions which may attack copper before reduction. Dilute hydrochloric acid (*1*) results in rapid and complete solution of the cuprous oxide and a slight attack on cupric oxide. Ammonium hydroxide, ammonium chloride, silver sulfate, and iodine were found to be unsuitable (*1*).

Table II. Conductivity of Aqueous and Organic Solutions

Solvent	Composition of Solutions per 100 Ml. of Solvent: Stannous chloride	Hydrochloric acid (sp. gr. = 1.19)	Conductivity 25° C.	Conductivity −10° C.
	Grams	*Ml.*	*Millimhos/cm.*	
Water	...	4	180	...
Water	4	4	190	...
Alcohol (95%)	...	4	7.4	4.8
Alcohol (95%)	4	4	6.6	3.6
Acetone	...	4	3.8	1.4
Acetone	4	4	8.0	6.5

Experiments were conducted to eliminate the attack of dilute hydrochloric acid on metallic copper and minimize the attack on cupric oxide. The strength of an acid is dependent on the degree of ionization, which is in turn dependent on the dissociation of the acid. Acids require water or similar polar mediums to enable ionization. Maximum ionization is obtained at infinite dilution. Although use of concentrated acid will decrease the total per cent ionization, its attack on the copper will increase. Therefore, the acid concentration is kept low but the water is replaced with an organic medium, ethyl alcohol, which reduces the ionization and conductivity of the solution. Alcoholic solutions of hydrochloric acid were found to give higher metallic copper figures, showing a decreased solution of copper. However, the results obtained for metallic copper decreased with increasing cupric ion content of the solution, indicating the need for a reducing agent to reduce any cupric oxide dissolved.

The selection of a reducing agent is restricted to a reagent soluble and active in dilute alcoholic hydrochloric acid solutions. After examination of a number of reducing agents, stannous chloride was found to meet the requirements. It is soluble in the alcoholic solution and quickly reduces cupric ion to cuprous ion. Further experiments on a number of commercial cuprous oxide samples containing very finely divided copper and cupric oxide showed that more accurate results and a decreased effect of time factor could be obtained with this solution by keeping the temperature low, particularly in cement copper pigments. The combined effect of lower temperature and inert atmosphere can be obtained by adding dry ice (solid carbon dioxide) to the reagent. Table II lists the conductivities obtained at various compositions of solutions and temperatures and illustrates clearly the reduced activity of the alcoholic solution.

REAGENTS

Denatured Alcohol, Formula 12A. To 1 liter of 95% ethyl alcohol, add 5 ml. of benzene. (Pure grain alcohol can be used in place of the denatured alcohol.)

Extraction Solution. Add 40 ml. of concentrated c.p. hydrochloric acid (sp. gr. 1.19) to 1 liter of the denatured alcohol. Mix thoroughly. Add 40 grams of c.p. fresh stannous chloride ($SnCl_2.2H_2O$) and stir until completely dissolved.

Ferric Chloride Solution. Add 75 grams of c.p. ferric chloride hexahydrate and 150 ml. of c.p. hydrochloric acid (sp. gr. 1.19) to 400 ml. of distilled water. Stir to complete solution, add 5 ml. of 30% hydrogen peroxide solution, and boil to remove excess.

Ceric Sulfate Solution. Mix 50 grams of ammonium hexanitrato cerate and 52 ml. of 1 to 1 sulfuric acid and dilute slowly to 1 liter with distilled water, stirring constantly. Allow to stand several days and filter off any suspended insoluble matter. Standardize by dissolving pure, analyzed copper foil free from oxide coatings in ferric chloride solution and titrating with the ceric sulfate solution, using *o*-phenanthroline indicator.

Indicator. *o*-Phenanthroline ferrous complex (ferroin), manufactured by G. Frederick Smith Co., Columbus, Ohio.

PROCEDURE

Add about 20 ml. of 4-mm. diameter glass beads to a 250-ml. Phillips conical beaker with lip. Weigh accurately, using tared glazed paper, a sample of suitable size depending on the metallic copper content. Use 1-gram sample for samples containing up to 10% metallic copper, 0.15-gram sample for high copper samples (80% metallic copper), and proportional amounts for intermedi-

ate mixtures, so that a titration greater than 50 ml. of the 0.1 *N* ceric sulfate is not required. Add 25 ml. of denatured alcohol to the beaker and swirl vigorously for 1 minute to disperse the pigment and break up any lumps. Add slowly 100 ml. of the extraction solution while swirling the flask. After the addition of the extraction solution, swirl the flask vigorously for 5 minutes, adding lumps of dry ice continuously during this time to lower the temperature of the solution to approximately 0° C. Break up any remaining lumps with a glass rod or policeman.

Filter off the metallic copper–cupric oxide residue on a filter pad as described below. Continue the addition of dry ice to the solution in the extraction flask to keep the temperature low. Wash the flask and residue with 150 to 200 ml. of denatured alcohol, using suction. Transfer the filter pad containing the residue to the original extraction flask and dissolve in 25 ml. of the ferric chloride–hydrochloric acid solution, maintaining an atmosphere of carbon dioxide above the sample by addition of dry ice. Heat on a steam bath to dissolve the copper. Add 50 ml. of distilled water and 3 drops of *o*-phenanthroline indicator. Titrate with the standard ceric sulfate until the color changes from orange to pale green. Calculate the metallic copper content as follows:

$$\frac{\text{Grams Cu per ml. ceric sulfate solution} \times \text{ml. ceric sulfate}}{\text{weight of sample}} \times 100 = \% \text{ metallic copper}$$

NOTES ON PROCEDURE

During the 5-minute swirling period, approximately 25 to 30 grams of dry ice are added in about 5-gram portions. The initial lumps of dry ice are volatilized rapidly, owing to the temperature of the solution. About 15 grams of dry ice are added in the first 2 minutes with a subsequent drop in temperature to 0° C. The remaining 10 grams volatilize more slowly and gradually lower the temperature to the vicinity of −10° C. These directions are not critical but merely serve as a guide line. During the filtration period, additons of dry ice to the flask should be continued to keep the solution cold until all the extraction solution has been filtered.

Table III. Determination of Metallic Copper in Synthetic Mixture

Weight Taken					
Metallic Cu[a]	Cu_2O[b]	CuO[c]	Cu Taken	Cu Found	Error
Gram	*Gram*	*Gram*	%	%	%
0.1250	...	...	...	98.8	....
0.0984	...	...	...	98.6	....
0.1402	...	...	...	98.5	....
....	0.100	...	...	0.48	....
....	0.100	...	...	0.50	....
....	0.100	...	...	0.50	....
....	...	1.00	...	0.0	....
....	...	1.00	...	0.0	....
0.0195	0.980	...	2.42	2.38	−0.04
0.0143	0.985	...	1.90	1.87	−0.03
0.0257	0.975	...	3.03	2.57	−0.06
0.0789	0.910	...	8.34	8.22	−0.08
0.1405	0.860	...	14.31	14.19	−0.12
0.1410	0.400	...	26.1	25.9	−0.20
0.1329	0.130	...	50.3	50.1	−0.20
0.1307	0.050	...	71.6	71.5	−0.1
0.0205	0.810	0.20	2.01	1.98	−0.03
0.0413	0.820	0.20	4.23	4.25	+0.02
0.0745	0.750	0.20	7.22	7.19	−0.03
0.1426	0.610	0.20	15.1	14.9	−0.20
0.0317	0.510	0.50	3.25	3.27	+0.02
0.0787	0.500	0.50	7.44	7.31	−0.13
0.1384	0.420	0.50	13.1	12.9	−0.20
0.1211	0.130	0.10	34.3	34.2	−0.10
0.1148	0.050	0.05	52.9	51.7	−0.40
0.1445	...	0.05	73.4	73.2	−0.20
0.1327	...	0.17	43.3	43.4	+0.10
0.1126	...	0.46	19.6	19.5	−0.10
0.1098	...	0.75	12.6	12.4	−0.20
0.1275	...	0.88	12.5	12.4	−0.10

[a] 325-mesh copper powder extracted with extraction solution used in procedure. Total reducing power of extracted copper powder is 222.3, equivalent to 98.8% Cu. This figure was used for metallic copper for calculation of % Cu taken.

[b] A commercial grade material containing 0.5% metallic Cu. Calculated copper was corrected for this amount.

[c] A 325-mesh reagent grade material with a 0.0% total reducing power.

Table IV. Analyses of Commercial Copper and Cuprous Oxide Pigments

Lot No.	29	1110	T-675	926	656	237	252H	3	1
Type	Grade A Cu_2O	Grade B Cu_2O	Copper Pigment	Grade A Cu_2O	Grade B Cu_2O	Grade B Cu_2O	Grade A Cu_2O	Copper Pigment	Copper Pigment
Copper, %	0.69	9.33	77.3	0.55	5.67	2.97	4.39	80.3	75.7
	0.71	9.46	77.1	0.61	5.50	2.94	4.30	80.1	76.0
	0.68	9.51	77.0	0.58	5.61	2.96	4.33	80.5	75.8
	0.71	9.55	77.4	0.58	5.60	2.90	4.29	80.5	75.6
	0.70	9.43	77.3	0.60	5.55	2.95	4.18	80.3	75.9
	0.68	9.50	77.4	0.61	5.65	2.90	4.35	80.4	76.0
Av.	0.69	9.45	77.3	0.59	5.60	2.94	4.31	80.4	75.8
Av. deviation, %	±0.01	±0.05	±0.1	±0.03	±0.05	±0.04	±0.05	±0.1	±0.1
Total reducing power	99.4	101.1	188.9	96.0	101.3	92.0	101.4	190.0	186.6
Total copper (electrolytically)	87.8	88.1	91.6	87.4	88.4	80.6	86.8	88.6	90.5
Cu_2O, %	97.8	79.8	15.0	94.7	87.7	85.3	91.7	9.1	16.0
CuO, %	0.3	9.7	1.3	3.4	6.1	2.4	1.3	0.2	0.7

The electrolytic type of cuprous oxide pigment (252H) was the only one which gave some difficulty in dispersing and breaking up lumps. The difficulty is due to the fact that a different coating is used on this pigment to prevent air oxidation. After swirling 5 minutes with the extraction solution, a number of small, undispersed lumps of cuprous oxide were clearly visible. However, these can be readily dispersed and dissolved by crushing them with a glass rod or a policeman. The solution should not be filtered until there is no evidence of lumps present.

Because of the extremely fine particle size of the metallic copper in some samples, care must be exercised in the filtration. The following method of filtration has been found satisfactory:

Prepare a layer of coarse asbestos on a glass or hard-rubber perforated disk contained in a Shimer filtering tube. Next, place a layer of fine asbestos over the coarse and pack firmly using suction. Wash the filter pad thoroughly with denatured alcohol. The pad is now ready for the filtration. If any copper passes through the pad, as is evidenced by a reddish color in the filtrate, discard the sample and repeat the analysis using a thicker and more tightly compressed pad.

RESULTS OF ANALYSIS

The metallic copper content of a number of synthetic mixtures was determined by the above procedure (Table III). The synthetic mixtures were prepared by weighing various amounts of metallic copper, cuprous oxide, and cupric oxide in such proportions as to obtain from 0 to 100% of each ingredient, to determine the effect of each constituent on the result for metallic copper. In only one case was the error greater than 0.3%. Although these results are satisfactory, it must be borne in mind that the ingredients were prepared separately and are not the same intimate mixtures that are found in commercial samples. Moreover, the copper powder is not so fine as many of the metallic copper particles found in the commercial samples.

Table IV lists the results of metallic copper determinations on a number of commercial antifouling pigments. Lots 29, 1110, 926, 656, and 237 are pyrometallurgical-type cuprous oxide pigments. Lot 252H is an electrolytic cuprous oxide. Lots T-675, 1, and 3 are copper pigments from cement copper. The average deviations are indicative of the degree of accuracy obtainable with this procedure. The total reducing powers and the total coppers were determined by the methods outlined in (*1*), except that the ceric sulfate was standardized with C.P. analyzed copper foil. The cuprous oxide and cupric oxide were determined by calculation. The increased accuracy of the method is indicated by the results obtained for lot 3. All the results for metallic copper obtained by methods previously discussed gave a considerably lower figure. This resulted in a negative figure for cupric oxide—for example, the method of (*1*) gave a figure of 70% metallic copper for lot 3 which resulted in a negative cupric oxide value of −12.9%. The average deviations obtained for the samples containing less than 10% copper was ±0.05%. For high copper samples, an average deviation of ±0.1% was obtained.

EXPERIMENTAL WORK

Effect of Contact Time and Temperature. The time of shaking in the extraction solution was varied from 2 minutes to 1 hour, maintaining the low temperature by continual additions of dry ice. High results were obtained on lots 926 and 29 when shaken only 2 minutes. Check results were obtained with all the samples when shaken in the extraction solution for from 5 minutes to 1 hour, provided the temperature was kept low. The effect of the decreased temperature is to eliminate the solvent action of the solution on the finely divided copper and greatly decrease the solvent action on the cupric oxide.

Effect of Atmosphere and Temperature. The determination of copper in an aqueous medium requires the use of an inert atmosphere above the solution to prevent rapid oxidation due to the high oxygen sensitivity of an aqueous acid solution of copper. The experiments with the proposed method show that the copper in the organic solution is insensitive to oxygen and the presence of an inert atmosphere is unnecessary. The important factor in the use of the alcoholic extraction solution, as demonstrated in Table V, is the use of low temperatures. Excellent results are obtained at low temperatures regardless of the surrounding atmosphere, and despite the fact that the copper is kept in contact with the extraction solution for one hour before filtering. At room temperature, however, low results are obtained in most cases when the copper and extraction solution are in contact one hour regardless of the atmosphere.

Effect of Solvent. The choice of a suitable solvent is limited by several factors. The solvent must remove the surface coating to disperse the pigment. The stannous chloride and cuprous chloride formed from the reaction of cuprous oxide and hydrochloric acid must be completely soluble in the solvent. These conditions eliminate most of the solvents except acetone and alcohol. The use of acetone results in rapid deterioration of the extraction solution and yields low metallic copper figures on the samples of high metallic copper content. The mixture of hydrochloric acid, stannous chloride, and denatured alcohol remains clear and water-white indefinitely. Replacing the alcohol with acetone results in the formation of a light yellow reaction product in 24 hours and a dark brown reaction product in several weeks. The result for metallic copper becomes progressively lower as the acetone extraction solution ages. No deleterious aging effects are found in the alcohol extraction solution.

Table V. Effect of Temperature and Atmosphere on Metallic Copper Determinations

Lot No.	29	656	252H	3
−10° C. with dry ice additions to the solution	0.70	5.63	4.30	80.2
−10° C. by placing extraction flask in alcohol–dry ice bath (no inert atmosphere)	0.69	5.58	4.35	80.5
CO_2 gas (room temperature)	0.52	4.67	4.25	79.1
N_2 gas (room temperature)	0.55	4.40	2.98	78.7
Room temperature (no inert atmosphere)	0.40	3.77	3.07	78.5

Samples remained in contact with extracting solution for 1 hour.

Acid Concentration. The concentration of 4 ml. of concentrated hydrochloric acid per 100 ml. of solvent used in the extraction solution represents the minimum quantity that will completely dissolve all the cuprous oxide in the samples tested. Doubling the acid concentration does not materially affect the results, owing to the low conductivity of the solution.

Stannous Chloride Concentration. Less than 2 grams or more than 6 grams of stannous chloride per 100 ml. of denatured alcohol in the extraction solution results in low metallic copper figures in a number of instances.

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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.

Determination of Magnesium in Aluminum Alloys

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The authors submit an analytical method of making the initial separation of magnesium hydroxide in the presence of other alloying constituents held in solution as complexes formed under controlled pH conditions. Final determination of magnesium may be a simple spectrophotometric measurement of the light transmission or optical density of the magnesium hydroxyquinolate in hydrochloric acid solution, the volumetric bromate-thiosulfate titration of magnesium hydroxyquinolate, or a gravimetric weighing as magnesium pyrophosphate.

THE increased production of complex aluminum alloys has created a difficult problem for the analytical chemist. Present aluminum alloys contain varying percentages of copper, iron, zinc, silicon, manganese, magnesium, chromium, nickel, titanium, and occasional associated impurities such as calcium, lead, tin, and bismuth. Spectrographic methods for the analysis of these complicated alloys have become increasingly popular, but only the larger laboratories have been able to obtain or can afford to purchase spectrographic equipment. The spectrograph does not eliminate the need of accurate chemical methods, since the spectrographer is dependent on the chemical laboratory for an accurate analysis of his spectrographic standards and the frequent checking of his results.

Since magnesium has a most pronounced effect on the physical properties of these alloys, it requires accurate analytical control. Standard basic procedures have been dependent on preliminary separation of the other metals with a final precipitation of the magnesium remaining. These procedures usually make an initial attack of the sample with sodium hydroxide, with addition of hydrogen or sodium peroxide if chromium is present. Samples of high silicon content require a special or modified treatment (*1*). The initial sodium hydroxide attack separates the aluminum as soluble sodium aluminate, leaving the other alloying metals as residuals. These are usually treated with hot, dilute hydrochloric acid to dissolve the magnesium, with a resulting solution of many other metals as well. Experienced analysts have recognized that the magnesium in the residue from the initial caustic attack is not always readily or completely soluble in hydrochloric acid. This may be due to a partial combination of the magnesium as magnesium silicide or other combinations with other alloying metals. Treatment of the residuals with nitric-sulfuric acids is effective in assuring complete solution of the magnesium, but further complicates subsequent separations (*2*).

The "ideal" analytical method indicated a complete solution of the alloy in hydrochloric-nitric-hydrofluoric acids and a direct precipitation of the magnesium. A survey of the literature offered no known reagent specific in a reaction with magnesium in acid solution and in the presence of aluminum and other alloying metals. The very low solubility of magnesium hydroxide indicated promise as an initial separation if the other metals could be held in an alkaline solution as complex compounds. Study and laboratory experiments proved that many of the complexes soluble in alkaline solutions could be formed by the addition of sodium tartrate, but manganese only by the addition of tartaric acid to the acid solution. Efforts to separate nickel quantita-

tively as a cyanide complex were unsuccessful until it was found that pH control was necessary. At a pH of approximately 7, the formation of a nickel cyanide complex soluble in alkaline solution is quantitative. The presence of the tartrates serves the dual purpose of forming soluble metal complexes and acting as a buffer for pH control in the formation of the soluble nickel cyanide complex.

After a final precipitation as the hydroxyquinolate, the magnesium may be determined by the well-known bromate-thiosulfate titration procedure (*3*). Spectrophotometric measurement, however, offers the decided advantages of eliminating the preparation and frequent standardization of volumetric solutions. Several references in the technical literature cover the conversion of magnesium hydroxyquinolate to ferric hydroxyquinolate and subsequent measurement (*4, 7, 9, 10*). The authors find it easier merely to dissolve the magnesium hydroxyquinolate in dilute hydrochloric acid and measure the light transmission or optical density, using a light wave length of 365 mμ. Using a cell having a light path of 1 cm., concentrations up to 6 micrograms per milliliter can be measured. The color is stable for several days and the plot of optical density *vs.* concentration obeys the Beer-Lambert law.

The simpler colorimeters using a tungsten lamp as a light source do not have sufficient sensitivity in the 365-mμ band. A mercury H-4 lamp with a narrow band filter may be used with colorimeters of the two-cell bridge-type circuit such as the Lumetron Model 402E, or the measurement may be made with a spectrophotometer such as the Beckman or the Coleman instrument.

When only an occasional analysis is to be made, the final precipitation of the magnesium may be made as the pyrophosphate with subsequent ignition and weighing. The accuracy of this method is equal to that of the other methods employed.

INSTRUMENTS

Spectrophotometric measurements were made using a Lumetron Model 402E fitted with an H-4 mercury lamp light source, a Sola constant-voltage transformer, a narrow-band 365-mμ glass filter and 1-cm. cells. Also used was a narrow band colorimeter of the authors' own construction having a tungsten lamp light source, a 929 vacuum photocell, and a slide-back potentiometric measuring circuit with two stages of electronic amplification in the null point galvanometer circuit.

REAGENTS

Sodium hydroxide solution, 200 grams dissolved and diluted to 1000 ml. Potassium cyanide solution, 300 grams dissolved and diluted to 1000 ml. Sodium tartrate solution, 300 grams dissolved and diluted to 1000 ml. Tartaric acid solution, 300 grams dissolved and diluted to 1000 ml.

Bromocresol purple indicator, 40 mg. dissolved in 100 ml. of ethanol.

8-Hydroxyquinoline reagent, 20 grams dissolved in 1000 ml. of isopropyl alcohol.

Alcohol-ammonia wash, 500 ml. of isopropyl alcohol, 480 ml. of water, and 20 ml. of ammonia water.

Sodium hydroxide wash, 100 ml. of sodium hydroxide solution diluted to 1000 ml.

Pyridine wash, 15 ml. of pyridine and 40 ml. of ammonia water in 1000 ml. of water.

Ammonium benzoate, 100 grams dissolved and diluted to 1000 ml.

Alizarin Red S, 0.10 gram dissolved in 100 ml. of glacial acetic acid.

Dilute acetic acid, 200 ml. of glacial acetic acid diluted to 1000 ml. Dilute hydrochloric acid, equal volumes of acid and water.

PROCEDURE

Spectrophotometric. Weigh a sample of 0.6 gram of alloys of 0.20 to 2.00% magnesium content, 1.2 grams if the magnesium content is below 0.20%. Place the weighed sample in a 500-ml. Erlenmeyer flask and add 20 ml. of dilute hydrochloric acid, warming, if necessary, to start reaction. When the reaction is complete add 10 ml. of nitric acid and heat to complete solution of the sample. In the presence of silicon in the alloy add hydrofluoric acid in 1- or 2-ml. portions, warming after each addition, until all silicon is dissolved and the solution is clear. Evaporate to drive off most of the free acids but avoid excessive formation of crystals, since these may be difficult to redissolve. A final volume of 10 ml. will usually satisfy these conditions.

Add 30 ml. of hot water, heat to boiling, and dissolve all salts as rapidly as possible. Add 20 ml. of sodium tartrate solution followed by 20 ml. of tartaric acid, boiling the solution vigorously after each addition. Add 8 to 10 drops of bromocresol purple indicator and add sodium hydroxide solution to the appearance of a distinct purple color, carefully avoiding any large excess. Keep at or near boiling during the addition of the sodium hydroxide solution. Add 10 ml. of potassium cyanide solution and boil one minute, then add 30 ml. of sodium hydroxide solution while keeping the solution at a vigorous boil until perfectly clear. Add 100 ml. of hot water slowly and hold just at boiling temperature about 1 or 2 minutes.

Remove the flask from the heat and swirl slowly. After slight cooling, the magnesium hydroxide usually appears as rather fine particles. Digest on a hot plate just below boiling temperature from 3 to 5 minutes. When the precipitate coagulates into rather large clumps, filter through a Whatman No. 30 or No. 40 or equivalent. Wash filter and flask thoroughly with hot 2% sodium hydroxide wash, taking care to remove as much of the aluminum salts as possible. Discard filtrate and washings.

Table I. Determination of Magnesium

	Reported %	Spectrophotometric %	Pyrophosphate %
Bureau of Standards			
No. 85	0.40	0.39	
		0.39	
		0.40	
		0.41	
		0.41	
		Av. 0.40	
No. 85a	1.58	1.57	1.57
		1.58	1.58
		1.57	1.59
		1.59	1.59
		1.58	1.59
		Av. 1.578	1.584
Aluminum Research Institute			
No. 39	0.21 av.	0.20	
		0.21	
		0.22	
		0.22	
		0.23	
		Av. 0.216	
No. 40	0.14 av.	0.14	
		0.13	
		0.13	
		0.15	
		Av. 0.137	
Alcoa spectrographic standards			
SA 104	0.89	0.88	
		0.88	
		0.89	
		0.89	
		0.90	
		Av. 0.888	
SAC 400	0.05	0.05	
		0.05	
		0.055	
		0.06	
		0.04	
		Av. 0.051	
SAC 118	0.50	0.51	
		0.50	
		0.50	
		0.52	
		Av. 0.508	
SSXA 142	1.53	1.53	
		1.53	
		1.53	
		1.51	
		1.54	
		Av. 1.528	

Composition of Samples Used

	85	85a	39	40	104	400	118	142
Cu	4.11	2.48	7.40	0.37	2.00	4.52	2.90	4.10
Sn	0.004	0.001	1.05	0.12	..	..	0.50	..
Pb	0.007	0.002	0.49	0.10	..	..	0.40	..
Zn	0.014	0.02	2.23	0.24	0.50	0.08	2.87	..
Si	0.46	0.11	1.88	5.58	6.79	2.35	2.43	0.12
Mn	0.56	0.66	0.21	0.08	..	0.09	0.21	..
Mg	0.40	1.58	0.21	0.14	0.89	0.05	0.50	1.53
Cr	...	0.23	0.36	0.09	..	..	..	0.19
Ni	...	0.41	0.83	0.10	..	0.17	0.09	2.07
Ti	0.02	0.016	0.11	0.10	..	0.08	0.09	0.11

Retention of some aluminum salts by the filter paper and occlusion by the magnesium hydroxide are unavoidable. Removal of these small traces of aluminum must be made by one of the three following procedures:

(*a*) Dissolve the washed magnesium hydroxide from the filter with 30 ml. of hot dilute acetic acid and wash the paper with hot water. Receive filtrate and washings in the flask in which the original precipitation was made. Hold volume to 60 to 75 ml. Add 10 ml. of ammonium benzoate solution (*6*) and bring just to boiling. Remove from hot plate and allow to stand 2 minutes. Filter on paper of medium texture, wash with warm water, and hold total volume to 100 to 125 ml. Discard paper, and reserve filtrate and washings.

(*b*) Dissolve the washed magnesium hydroxide from the filter with 30 ml. of hot dilute hydrochloric acid and wash paper with hot water, holding volume to 60 to 75 ml. Add 2 drops of bromocresol purple indicator and carefully neutralize with ammonia water to the appearance of a faint purple color. Add 1 ml. of Alizarin Red S solution (*3*) followed by 2 ml. of ammonia water. Heat to temperature of approximately 90° C., remove from heat, and allow to stand until the appearance of a red precipitate. Filter on medium texture paper and wash with warm water. Save the filtrate, and discard filter paper.

(*c*) Follow procedure given under (*b*) through neutralization with ammonia water. Add 2 ml. of pyridine and warm to 45° to 50° C. Remove from hot plate, swirl flask thoroughly several times, and allow to stand a few minutes. The aluminum pyridine complex forms a white gelatinous precipitate. Filter on a paper of usual type and wash with pyridine-ammonia wash water, holding volume to approximately 125 ml.

Remove the small residual traces of aluminum by one of the three procedures given and precipitate the magnesium as the hydroxyquinolate. If procedure (*a*) has been followed, neutralize the solution with ammonia water, using a few drops of bromocresol purple as indicator. To the neutral solution add a minimum of 5 ml. of the 8-hydroxyquinoline reagent plus 1 ml. for 0.1% of magnesium above 0.5% anticipated in the sample. (On samples of low magnesium content the addition of 2 or 3 ml. of tartaric acid solution prior to the neutralization with ammonia water will facilitate the subsequent precipitation of the magnesium hydroxyquinolate.) Add 10 ml. of ammonia water and heat to a vigorous boil. Then hold just below boiling for 5 or 10 minutes or until the precipitate begins to settle. Remove from hot plate and allow to stand an additional 5 minutes.

Filter on Whatman No. 40 or equivalent and wash thoroughly with the alcohol-ammonia wash to remove all excess reagent. Dissolve the magnesium hydroxyquinolate precipitate from the filter with 40 ml. of hot dilute hydrochloric acid and wash paper with hot water. Receive the filtrate and washings in a 200-ml. volumetric flask, Kohlrausch type preferred. Cool thoroughly and dilute to mark. Pipet accurately 20 ml. to a second 200-ml. volumetric flask, add 10 ml. of dilute hydrochloric acid, dilute to mark, and measure transmission or optical density. On alloys of low magnesium content, it is preferable to measure without the second dilution and calculate accordingly.

Preparation of Spectrophotometric Graph. Dissolve 0.5 gram of pure magnesium metal in 50 ml. of dilute hydrochloric acid and dilute to 1 liter. Measure accurately from a buret 30 ml. into a 500-ml. Erlenmeyer flask, dilute to 125 ml., add 20 ml. of 8-hydroxyquinoline reagent and 12 ml. of ammonia water, precipitate, and wash as directed above. Dissolve the precipitate with 40 ml. of hot dilute hydrochloric acid and receive the filtrate and washings in a 500-ml. volumetric flask. Cool and dilute to mark. Measure accurately into 100-ml. volumetric flasks 2-, 4-, 6-, ...20-ml. volumes, add 10 ml. of dilute hydrochloric acid, dilute to mark, and measure transmission or optical density in cells of 1-cm. light path, using light of 365-mμ wave length. These quantities are equivalent to 0.20, 0.40, 0.60.....2.00% magnesium content on the 0.6-gram sample weight specified. Transmission *vs.* concentration plotted on semilog paper should give a straight line. Coleman spectrophotometer paper has been found of a convenient size and arrangement for this and similar graphs.

Bromate-Thiosulfate Method (*3*). Using a sample weight of 0.5 or 1.0 gram according to the magnesium content of the alloy, follow the preceding procedure through the final precipitation and washing of the magnesium hydroxyquinolate. Dissolve the precipitate from the filter with 30 ml. of hot dilute hydrochloric acid, receiving the filtrate and washings in a 500-ml. Erlenmeyer flask. Cool thoroughly, dilute to 125 to 150 ml., add 5 drops of carbon tetrachloride, and with constant swirling of the flask add the standardized potassium bromate solution from a buret until the carbon tetrachloride takes on a faint reddish color. Add 10 ml. of potassium iodide solution and titrate the liberated iodine with standardized sodium thiosulfate to a pale straw color. Add a few milliliters of starch solution and continue the titration to the disappearance of the blue color. Add the last few drops of thiosulfate slowly to ensure reaction with any small amount of iodine held by the carbon tetrachloride. The bromate solution may be standardized by precipitation of known amounts of magnesium as the hydroxyquinolate and titration in the usual manner.

Gravimetric Pyrophosphate Method (*5*). Using 0.5- to 1.0-gram sample weight, precipitate the magnesium hydroxide and wash as directed. Dissolve the precipitate from the filter with 30 ml. of hot, dilute hydrochloric acid and remove the residual aluminum by the use of pyridine as given under procedure (*c*). Receive the filtrate from the pyridine separation in a 400-ml. beaker and make just acid to methyl red indicator, using dilute hydrochloric acid. Add 10 to 20 ml. of saturated diammonium phosphate solution with constant stirring. Add ammonia water slowly with continued stirring until no further precipitation is apparent, then add an excess of ammonia water equivalent in volume to 5% of the original volume. Cover and allow to stand overnight, preferably in an ice box. Use a beaker free of scratches and avoid scratching with the glass stirring rod. Filter and wash with cold water containing 2% ammonia water. Ignite in a weighed porcelain crucible until the precipitate is completely white. After burning off the filter paper, final ignition in a muffle furnace at 1050° to 1150° C. is preferable. Factor = 0.2184.

EXPERIMENTAL CHECKS

Since various metals are used as alloying additions in aluminum alloys or may occur as impurities, synthetic samples of various compositions were prepared. These consisted of the chlorides of nickel, chromium, iron, copper, titanium, calcium, tin, zinc, manganese, aluminum, and lead nitrate, together with known amounts of magnesium as the chloride. These synthetic samples were then analyzed by the spectrophotometric procedure. Magnesium recovered agreed with the known amount present within the limits of experimental error, indicating the noninterference of these metals. Analytical results obtained on two Bureau of Standards samples, two Aluminum Research Institute exchange samples, and four Aluminum Company of America spectrographic standards are reported in Table I. In the certificate furnished with the Alcoa spectrographic standards, the purchaser is warned that: "These standards are prepared and standardized for use in spectrographic analysis by methods similar to those of the Aluminum Company of America. They are not necessarily suitable for use in analytical methods involving the use of other sample forms or procedures."

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Determination of Menthol in Peppermint Oil

Acetic Anhydride and Pyridine as Reagent

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THIS study was undertaken to meet the need in a research program on peppermint oil production for simplification and increased accuracy in methods used for the quantitative determination of menthol. The method of Power and Kleber (*7*), generally accepted in the aromatic industry for that compound and "official" in the United States Pharmacopoeia, is both time-consuming and of questioned reliability, since variable results on identical samples of oil have been obtained all too frequently by it in different laboratories.

Brignall (*1*) described a new procedure for the hydroxyl group based on the use of an acetylating mixture consisting of acetic anhydride and *n*-butyl ether. In peppermint oils free menthol determinations by this method have averaged about 3% lower than those done by the method of Power and Kleber. Christensen and Pennington (*2*) worked out a method involving the use of acetyl chloride in determining menthol in peppermint oil. By it, results of menthol determinations in this laboratory agree very well with those obtained by the Brignall procedure but fall distinctly low in comparison with those obtained by the official method. Other methods—viz., one by Delaby, Sabetay, and Brengnot (*3*), one by Freed and Wynne (*4*), and one by Ogg, Porter, and Willits (*5*), each making use of a mixture of pyridine and acetic anhydride—have been proposed for the analysis of primary and secondary alcohols with application of heat. A micromethod, too, has been proposed by Petersen, Hedberg, and Christensen (*6*) using the same reagent without application of heat for determination of the hydroxyl content of pure organic compounds. The authors recently applied this last-mentioned technique on the macro scale for the determination of free menthol in peppermint oils.

ANALYTICAL PROCEDURE

The necessary reagents are: C.P. acetic anhydride, pyridine C.P. and water-free, and sodium hydroxide 0.5 *N* and carbonate-free.

An approximately 0.6-gram sample of oil is introduced into a weighed 7.5-cm. (3-inch) test tube by means of a dropper and its weight again taken accurately to find the weight of sample used. Approximately 0.5 gram of acetic anhydride is introduced into the tube, which is then reweighed. Following the addition of 0.5 cc. of pyridine, the tube is sealed with a cork which previously has been dipped in melted paraffin. The tube is immediately shaken once, set aside at room temperature for 48 hours, then opened and placed in an Erlenmeyer flask. Fifty cubic centimeters of water are added and the solution is titrated with standard sodium hydroxide. Near the end of the titration, flask and contents are heated for a few minutes to ensure complete hydrolysis of the excess acetic anhydride and then titration is carried to the end point of phenolphthalein as shown by persistence of the pink color for 1 minute. A blank titration is carried out at the same time to determine the volume of standard base required to neutralize the acid derived from 1 gram of acetic anhydride. Another sample is weighed and titrated with standard alcoholic sodium hydroxide with phenolphthalein as indicator to determine the amount of free acid in the peppermint oil. The per cent of free menthol is then calculated by the formula

$$\% \text{ free menthol} = \frac{(A \times R - B_1 + B_2)N \times 156.16 \times 100}{W}$$

in which

A = weight in grams of acetic anhydride used
R = ml. of standard base required to neutralize the acid derived from 1 gram of acetic anhydride
B_1 = ml. of standard base required to neutralize the remaining acid
B_2 = ml. of standard base required to neutralize the free acid of the sample
N = normality of standard base
W = weight of sample in milligrams

ANALYTICAL RESULTS

Free menthol was determined on samples of mint oil obtained by steam-distillation and refined by petroleum ether extraction.

Table I shows that an acetylation period of more than 24 hours is necessary and that one of 28 to 32 hours is ample for maximum values.

At least 100% in excess of the theoretical amount of acetylating agent is required (Table II).

The amount of pyridine used may vary within a rather wide range but the ratio of acetic anhydride to pyridine must not be less than 5 to 5 (Table III).

In Table IV each value by the Christensen and Pennington and the official methods is the average of two determinations; each value by the authors' method is the average of two or more determinations. Results by the official method and by the authors' method are in close agreement, while results by the Christensen and Pennington method are from 1 to 4% lower.

Finally the authors' method was used for the recovery of menthol added in varying amounts to 500 mg. of peppermint oil containing 50.6% of free menthol. Recovery values shown in Table V, from single determinations, are considered satisfactory.

Table I. Effect of Variations in Length of Acetylating Period

Acetylation Period *Hours*	Free Menthol Found[a] %
4	44.7
8	46.3
12	46.3
16	47.9
20	48.0
24	47.9
28	50.0
32	50.0
36	49.1
40	49.5
44	50.1
48	49.4

[a] Each value from a single determination.

Table II. Effect of Variations in Amount of Acetylating Agent Used

Acetic Anhydride Used, % of Theoretical Requirement	Free Menthol Found, %
106	38.9
158	47.8
169	47.9
203	49.8
230	50.1
252	50.1
287	49.5

Table III. Effect of Varying Acetic Anhydride–Pyridine Ratio

(Acetylating period 48 hours, room temperature, and at least 100% excess acetic anhydride)

Acetic Anhydride–Pyridine Ratio	Free Menthol Found, %
Without pyridine	11.5
5:1	51.2
5:2	50.1
5:3	51.0
5:4	51.4
5:5	51.1
5:7.5	50.1
5:10	49.9
5:15	49.1
5:20	48.8

Table IV. Results by Different Procedures

Sample	Christensen and Pennington % of menthol	Christensen and Pennington Average deviation	Official or Power and Kleber % of menthol	Official or Power and Kleber Average deviation	Authors % of menthol	Authors Average deviation
A	52.0	0.3	54.0	0.2	53.9	0.1
B	52.6	0.1	53.2	0.5	54.2	0.2
F	51.4	0.2	52.2	0.3	52.4	0.2
G	51.4	0.4	53.1	0.4	53.3	0.1
7	51.2	0.2	52.8	0.6	52.7	0.2
7A	52.1	0.7	54.7	0.1	54.8	0.1
D7	53.1	0.2	56.0	0.6	56.1	0.0
D7A	54.0	0.8	58.0	0.2	57.6	0.1
82	51.0	0.1	51.9	0.4	51.2	0.0

Table V. Recovery of Menthol

Menthol Added *Mg.*	Menthol Actually Present *Mg.*	Menthol Found *Mg.*	Recovery %
60.7	318.7	318.7	100.0
50.7	303.7	304.3	100.2
106.1	363.1	361.5	99.8
102.3	350.3	347.2	99.1
151.6	366.6	363.3	99.1
146.8	375.8	374.6	99.7
184.4	388.4	383.7	98.8
193.0	402.0	395.7	98.5

SUMMARY

From the standpoint of time requirement and reproducibility of results, a very satisfactory procedure has been developed for the determination of free menthol in peppermint oil. It is based upon the utilization of a mixture of acetic anhydride and pyridine. The necessary acetylation period is somewhat longer for menthol than is required by the microprocedure with the same mixture for other alcohols unaccompanied by such a mixture of compounds as that which characterizes peppermint oil. The requirement for acetic anhydride is at least 100% in excess of the theoretical amount. Since the menthol content of peppermint oil varies with the several factors pertaining to production and time of harvesting, it is necessary to add a substantial excess of this reagent. The amount of pyridine used may vary within a rather wide range, but the ratio of acetic anhydride to pyridine must not be greater than 1 to 1. A wider ratio necessitates a longer acetylation period. For peppermint oils containing free acid, the values thus obtained should be corrected.

From this series of experiments it is clear that the Power and Kleber, or official, method for free menthol in peppermint oil is capable of yielding very satisfactory results, if the details of manipulation as given in the U. S. Pharmacopoeia are closely followed. The method devised by the authors, however, involving the use of acetic anhydride and pyridine as acetylating agents, is both more economical of reagents and substantially less time-consuming per sample, particularly when a fairly large number of samples of oil are involved. Samples set aside for acetylation require no attention during the acetylation period. Duplicate results determined by the authors' method check more closely than those by the official method.

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Accelerated Aging Test for Insecticidal Aerosols Containing DDT

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The introduction of DDT into the liquefied-gas aerosol has created the problem of stabilizing the aerosol solution and preventing corrosion of the container. The ease with which hydrochloric acid is liberated from DDT in the presence of some iron salts has made necessary the development of an accelerated aging test for studying the effect of the different aerosol constituents on this reaction. A simple pressure test tube and a method of running a test are described. The rate of decomposition varies greatly, depending mostly on the solvents used. Certain combinations have been developed which appear to be satisfactory.

THE first insecticidal aerosol (*2*) used by our armed forces consisted of a solution of pyrethrum and sesame oil in dichlorodifluoromethane (Freon-12). This aerosol was very effective against mosquitoes, but the addition of DDT was found to increase its toxicity to flies and other insects (*4*). The incorporation of DDT in the aerosol presents several problems, including corrosion of the iron container and formation of tarry materials by decomposition of some of the aerosol constituents.

DDT tends to liberate hydrochloric acid in the presence of some metals and their salts (*1*). Ferric chloride is a particularly good catalyst when the DDT is dissolved in some solvents, but in others very little action takes place. The solvent combination for the DDT aerosol solution is therefore very important. Since DDT is only slightly soluble in Freon-12, some cosolvent must be used to keep even as little as 3% in solution. The choice of a cosolvent must take into consideration its effect on the decomposition of DDT in an iron aerosol bomb. In order to study some of these effects an accelerated aging test was developed. The method of making the test and some results are reported in this paper.

APPARATUS

A simple pressure test tube was devised for these tests. A heavy glass tube was fitted to a tire valve as shown in Figure 1. The construction is described as follows: The frame, 1, was cut from $^1/_2$-inch brass pipe and threaded on the inside of each end with $^3/_8$-inch pipe threads. A standard $^3/_8$-inch brass pipe plug, 2, was drilled, and a tire-valve stem, 3, was soldered in place, about 0.6 cm. (0.25 inch) of the stem extending through the plug. This extension passed through the neoprene washer, 4, and prevented the flow of the rubber, which was under pressure, from closing the hole. The glass test tube, 5, was made from tubing having an inside diameter of 10 mm. and an outside diameter of 15 mm., and was 15 cm. (6 inches) long. It was sealed at one end, cut at right angles and fire-polished at the other end, and then annealed. The last step is very important. A calibration mark was etched on with a small grinding tool at a point where the tube would contain 10 grams of solution. The test tube was held in place against the washer by another $^3/_8$-inch brass pipe plug, 6. A 0.47-cm. ($^3/_{16}$-inch) depression was turned in the plug to accommodate a leather washer, 7, as a pad to protect the glass. The test strip, 8, was usually iron. Its size was 7.5 × 0.6 × 0.04 cm. (3 by 0.25 by $^1/_{64}$ inch), affording twice the surface per unit volume of solution occurring in a 0.45-kg. (1-pound) aerosol bomb.

Different types of valve cores were used. Those having neoprene gaskets and valve seats were best. A special type having a stiff spring, such as is used in the hydraulic system on airplanes, gave the least leakage. An ordinary valve cap was used as an added precaution.

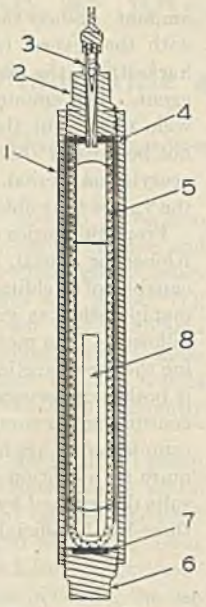

Figure 1. Pressure Test Tube for Testing DDT Aerosols

TESTING PROCEDURE

All the apparatus must be carefully cleaned to eliminate the possibility of catalysts that might cause decomposition of DDT. Moisture, hydrochloric acid, or iron salts of any kind must be avoided.

The glass tubes were cleaned in a hot nitric and sulfuric acid bath, rinsed at least 15 times with tap and distilled water, and dried at 110° C. The neoprene washers were boiled in distilled water, washed with pure acetone, and dried at 60° C. The valve stems were cleaned with chloroform and pure acetone and dried at 110° C. The valve cores were washed quickly in chloroform and then in acetone and dried at 60° C.

Most of the nonvolatile materials tested were dried in a vacuum while being heated to 60° C. for at least 30 minutes, and later were stored in a vacuum desiccator. Some were used as received to study the effect of undried materials. Freon-12 was always used as received.

The iron test strips were of the same material used for the manufacture of the aerosol bombs. They were kept under light oil, but some corrosion occurred and had to be removed. The method of cleaning the metal strips affected the results of the tests. Wire brushing, acid treatments, or tumbling with sand was not satisfactory. Apparently certain catalysts were introduced which give erratic results. Fine emery cloth was found to be the best material for cleaning. The method was slow, but uniform results were obtained.

All the nonvolatile materials were weighed into the clean test tubes, the metal strip was added, and the apparatus was assembled. Moderate pressure of the glass tube on the neoprene washer prevented appreciable leakage of Freon for more than 2 months. The Freon was introduced up to the mark all at once from a warm supply to obtain a pressure head. This procedure trapped some air, so that conditions were similar to those in an aerosol bomb, and eliminated condensed moisture that might be carried into the apparatus. The tubes were then placed in an oven at 60° C. They were examined at intervals for corrosion or changes in the system.

The formulas of the aerosol solutions used for these tests are presented in Table I.

Table I. Composition of Basic Formulas Tested

	Per Cent by Weight in Following Formulas											
	1	2	3	4	5	6	7	8	9	10	11	12
Constituent												
Insecticides												
Pyrethrum extract (20%)	2	2	2	2	2	2	2	..	2	2	2	2
DDT	3	3	3	3	..	3	3	5	3	3	2	3
Lethane[a]	..	..	..	5	..	..	..	..	..	...	...	..
Thanite[b]	..	..	5	..	..	..	..	..	..	...	...	..
Synergists												
Sesame oil	..	..	..	..	8	..	..	..	..	...	...	..
Synergist 312[c]	..	..	..	..	..	3	..	..	..	...	...	..
Solvents												
Methylene chloride	..	..	..	..	..	..	..	..	30	...	...	..
APS-202[d]	..	7	..	..	..	12	..	..	..	...	8	12
Cyclohexanone	5	..	5	5	..	..	..	5	..	5	...	..
Lubricating oil (No. 30)	5	..	..	..	..	..	5	..	5	5	...	..
Acetone	..	..	..	..	..	..	..	35	..	...	...	..
Isophorone	..	..	..	..	..	..	5	..	..	...	...	..
Velsicol[d]	..	..	..	..	..	..	..	5	..	...	...	..
Inhibitors												
Dioleyl malate	..	..	..	..	..	..	..	..	..	0.03	...	..
Degras fatty acids	..	..	..	..	..	..	..	..	..	...	0.03	..
Propylene oxide	..	5	..	..	..	..	..	..	..	...	...	..
Liquefied gases												
Freon-12[e]	85	83	85	85	90	80	85	..	60	85—	88—	83
Methyl chloride	..	..	..	..	..	..	..	50	..	...	...	..

[a] β-Butoxy-β'-thiocyanodiethyl ether.
[b] Bornyl and fenchyl thiocyanoacetates mixture.
[c] 3-Hexyl-5-piperonyl-2-cyclohexen-1-one and 6-carboethoxy-3-hexyl-5-piperonyl-2-cyclohexen-1-one mixture.
[d] Alkylated naphthalenes from petroleum.
[e] Dichlorodifluoromethane.

RESULTS

At first all tests were terminated at the end of one month The strips of metal were washed with hexane, dried, and weighed. Hexane was used because it does not remove the tars that are often formed. However, the gain in weight which is a combination of the corrosion products and polymerized materials which often occur simultaneously did not appear to be a good criterion of stability. Later the tests were continued until corrosion or tar formation started. The time interval was used as the basis of comparison, and it is on this information that the following statements are based.

The combination tested most frequently (No. 1) contains pyrethrum extract, DDT, cyclohexanone, and lubricating oil dissolved in Freon-12. The stability of the solution depends first on the method of manufacturing the pyrethrum extract. Four kinds of pyrethrum extract were tried in this formula, and it was learned that the extracts having the most naturally occurring inhibitors are best. Various types of lubricating oils also had a considerable effect. Aromatic base oils seemed to be the best, and some of the oils tested may have contained inhibitors. Three grades of DDT were used in combination 1. A purified grade of DDT is generally better than a technical grade; some technical grades are better than others. Cyclohexanone appears to reduce the stability of the mixture. Only freshly distilled anhydrous material can be used and this is variable. This mixture usually breaks down in less than one month at 60° C.

The thiocyanate insecticides (Nos. 3 and 4) are not so stable as pyrethrum extracts in a DDT aerosol solution. The mixture of pyrethrum and sesame oil (No. 5) without DDT is stable over very long periods, and has never caused corrosion of iron nor tar formation. Synergist 312 (No. 6) has shown poor stability in two tests, causing tar formation in 26 days.

A combination such as No. 12 can be handled most easily, and gives very good results in these tests. It contains pyrethrum extract, DDT, and an aromatic petroleum fraction in Freon-12. Various proportions have been tested and none has broken down before 50 days, while some have run more than 100 days. This aromatic petroleum cosolvent, a by-product in the manufacture of high-octane gasoline, consists mostly of polymers of alkylated naphthalenes and anthracenes, but the exact composition is not known.

Two tests with isophorone (No. 7) show that it forms a fairly stable solution, causing tar formation in 52 days. Acetone (No. 8) in combination with DDT in methyl chloride causes definite corrosion of iron, but no tar. Methylene chloride (No. 9) is a very good diluent for Freon-12 (*3*) and a good cosolvent to keep DDT in solution, but is not so stable in the aerosol mixture as would be desired. The period before decomposition was 44 days.

Propylene oxide (No. 2) is both an excellent solvent for DDT and a stabilizer. Its ability to accept nascent hydrochloric acid appears to stabilize the DDT aerosol solution. No corrosion nor tar formation has occurred in tests running as long as 150 days. The combination (No. 2) of the aromatic petroleum fraction and propylene oxide appears to give the most stable DDT aerosol solution. Propylene oxide has the disadvantage of being highly flammable and slightly toxic, so that considerably more care must be used in manufacturing the aerosol bomb. It is not flammable when mixed with Freon in the proportions needed.

Dioleyl malate (No. 10) appears to give added stability to the solution in some cases. Degras fatty acids (No. 11) give no protection.

Freon-12 appears to give a more stable solution than methyl chloride. Not many tests have been made on methyl chloride, since it is not used in the military aerosol bomb.

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Determination of Traces of Acetylene in Liquid Oxygen in Rectifying Columns

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A modified method for determining very small amounts of acetylene in liquid oxygen from air-rectifying columns is presented. As acetylene is dangerous in these columns and will sometimes explode violently, studies were made of the acetylene content when (1) different lubricating oils are used, (2) calcium carbide is stored near an oxygen plant, (3) liquid oxygen is periodically drained from the columns and discarded, (4) the air intake location is changed, and (5) an acetylene plant is located in close proximity to an air-reduction plant.

IT IS generally believed that explosions in the pure oxygen pot of rectifying columns producing oxygen from liquid air are attributable to acetylene. Acetylene may be present in the crude air or may be formed from the breakdown of the lubricating oil in the air compressor. As oxygen boils at −183° C. and acetylene freezes at −81° C., nearly all the acetylene entering the column will remain there.

However, it is distinctly possible that other hydrocarbon materials can produce explosions in rectifying columns, because practically all hydrocarbon materials will burn with oxygen and many will explode with liquid oxygen. Some detonator is required to set the explosion off, although acetylene and other materials may detonate spontaneously. All this goes to show the great danger in the presence and accumulation of hydrocarbon materials in liquid oxygen condensers.

From the standpoint of safe operation, a method for determining traces of acetylene in liquid oxygen was needed. Since many oxygen plants do not have a trained chemist available for analytical work, it was desirable that the method developed be one which could be used by plant operators.

LITERATURE REVIEW

Practically nothing on the subject has been published in this country, although many Russian papers deal with this work, and some German articles and several English papers have been reported.

Pollitzer (*4*) states that about 80% of the acetylene in the air will remain in the apparatus. He cites as an example that, in a plant making 100 cubic meters of oxygen per hour, using air that contains 5 parts per million of acetylene, about 1 kg. of acetylene will enter the apparatus in the course of 14 days and about 0.8 kg. will remain. The exact quantity of acetylene needed to produce an explosion is not accurately known. A few grams suffice, under certain conditions, to produce a strong local explosion.

Burbo (*1*) discusses the dangerous deposition of solid acetylene in the condensers of the oxygen column. He gives the vapor pressure of solid acetylene as from 89° to 105° Kelvin. If all oxygen is continuously evaporated from the main condenser, a maximum of 0.184 cc. of acetylene is evaporated per cubic meter of oxygen, corresponding to a maximum concentration of 0.037 p.p.m. of acetylene in the incoming air, in excess of which solid acetylene will accumulate.

Coulson-Smith and Seyfang (*2*) describe a colorimetric method based on the color of copper acetylide in colloidal solution (Ilosvay's solution). A series of mixtures of air and acetylene was prepared and 100 ml. of each were passed through ammoniacal cuprous chloride solutions. The resulting cuprous acetylide solutions were then matched by running measured amounts of a standard iron solution into a 5% potassium thiocyanate solution. One of the present authors checked these results, using a water solution of acetylene made from carbide, purifying it to remove phosphine and hydrogen sulfide, and passing the gas through distilled water. The acetylene content was determined by adding 10 ml. of 0.01 *N* silver nitrate, filtering off the silver acetylide, and back-titrating the remaining silver nitrate with 0.01 *N* potassium thiocyanate. The value obtained was 0.14 ml. of acetylene per ml. of water. Next, various amounts of the acetylene water were run into ammoniacal cuprous chloride solution (described below) and the color was obtained by the iron solution and potassium thiosulfate of Coulson-Smith and Seyfang. Excellent checks were obtained (see Table I).

When determining acetylene in liquid oxygen, the gasified oxygen cannot be bubbled directly through the Ilosvay solution (ammoniacal cuprous chloride), since it will oxidize the colorless cuprous solution to a blue cupric compound and hence will interfere with the color comparison. Obviously the sample of liquid oxygen must first be gasified and the acetylene frozen out.

Oks (*3*) describes a condenser for such a purpose. He also used a large copper funnel of 5000-ml. capacity, tapering down to a neck of 500-ml. capacity. The sample of liquid oxygen was boiled down to 500 ml. A stopper was then inserted in the neck, water poured in to make an ice seal, and the balance of the gasified oxygen run through the condenser.

The authors have modified the methods of Coulson-Smith and Seyfang and of Oks (the best Russian work), for the determination of acetylene in liquid oxygen.

EXPERIMENTAL WORK

Work of Coulson-Smith and Seyfang (*2*) was checked (Table I).

The authors used the iron solution as a standard in their first tests, but calibrated a Corning glass filter No. 348 (Table II) for a permanent standard. The solution used was prepared as follows:

CUPROUS CHLORIDE. Twelve grams of cuprous chloride were dissolved in 300 ml. of distilled water and 135 ml. of concentrated ammonium hydroxide were added, and then stirred. The solution was transferred to a bottle in which some copper wire had been placed.

HYDROXYLAMINE HYDROCHLORIDE SOLUTION. Seventy grams of hydroxylamine hydrochloride were dissolved in 300 ml. of warm water and placed in a stoppered bottle.

STARCH SOLUTION. Soluble starch (2.5 grams) was mixed in 5 ml. of cold water poured into 300 ml. of boiling water. This was boiled for 2 minutes, cooled, and diluted to 500 ml.

To 20 ml. of the cuprous chloride were added 30 ml. of hydroxylamine hydrochloride and 20 ml. of starch solution. This was placed in a 100-ml. Nessler tube and 30 ml. of distilled water were added, followed by the acetylene water. The starch was used in order to keep the cuprous acetylide precipitate in a colloidal state for easier color comparison.

Another method of determining the acetylene is to bubble the gasified sample through an ammoniacal silver nitrate solution, filter the silver acetylide precipitate off, dissolve it in nitric acid, and titrate the silver with potassium thiocyanate. Oks (*3*) shows that the results obtained by this method are about five times as low as those obtained with the ammoniacal cuprous chloride solution.

The authors decided that the ammoniacal cuprous chloride method was the better one for their purpose.

Table I. Determination of Acetylene

C_2H_2 Water	Ferric Alum to Match Color (0.35-Ml. Blank)	Equivalent Ferric Alum	C_2H_2 Content of Water	
			Coulsen-Smith and Seyfang	Eddy
Ml.	*Ml.*	*Ml.*	*Ml.*	*Ml.*
0.1	0.50	0.15	0.015	0.014
0.2	0.62	0.27	0.027	0.028
0.3	0.74	0.39	0.039	0.042
0.4	0.87	0.52	0.052	0.056
0.5	1.05	0.70	0.070	0.070
0.6	1.22	0.87	0.087	0.084
0.7	1.37	1.02	0.102	0.098
0.8	1.50	1.15	0.115	0.112

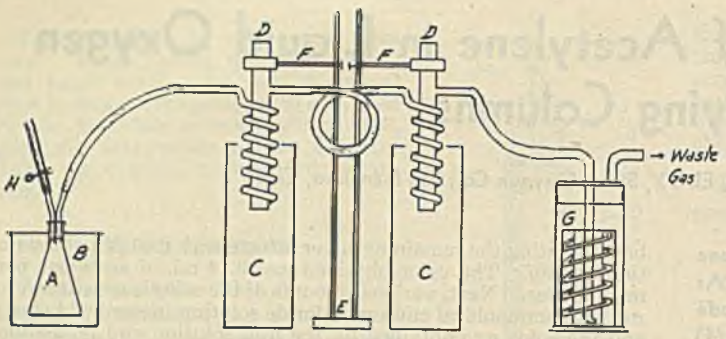

Figure 1. Apparatus for Acetylene Test

A. Erlenmeyer flask
B. Pyrex beaker
C. Pyrex thermos bottles
D. Oks condensers
E. Double ring stand
F. Buret clamps
G. Milligan absorption bulb
H. Pinchclamp

The funnel described by Oks (*3*) was found too cumbersome in use. The ice plug blew out on the trial runs, thus making a better arrangement desirable.

Finally, an Erlenmeyer flask was placed in a 100-ml. beaker and packed with rock wool. The sample of liquid oxygen was placed in the flask, stoppered with a two-hole rubber stopper, and the gasified oxygen passed through two of the Oks condensers, which were immersed in liquid oxygen (see Figure 1 for details of this equipment). A 250-ml. Erlenmeyer flask was used when testing samples above 0.7 p.p.m. A larger sample was taken when dealing with lower concentrations.

After all the oxygen had vaporized (evidenced by melting of the frost on the rubber tubing), the first condenser was lifted out of its cooling liquid and examined for recondensed oxygen. Oxygen recondenses if the condensers are inserted too far into the liquid oxygen. If any was present, it was slowly vaporized off by lifting the condenser out of the liquid, but without removing the vacuum flask, since evaporation would then be too fast and the acetylene would be carried off. This was repeated for the second condenser.

Next the absorption bulb, filled with 150 ml. of Ilosvay solution, was connected to the last condenser; the vacuum flasks were removed, and a nitrogen supply was connected to the Erlenmeyer flask at low pressure. The pinchclamp was removed and nitrogen was bubbled through for a half hour.

When the first part of the gas was passed through, the solution turned blue owing to the oxygen present, but this soon disappeared as the excess hydroxylamine hydrochloride reduced it to the colorless form. A pink to red color was imparted to the solution by the acetylene, depending upon the amount present.

The absorption bulb was removed and the color compared with the comparator part of the colorimeter. A 100-ml. tube of distilled water was placed over the glass to simulate the conditions of the unknown. The glass was calibrated by means of the ferric alum solution. Since only 100 ml. of the 150 ml. of solution from the absorber were used, when 100 ml. of solution matched the glass filter, the ferric alum equivalent of the whole solution would be 150/100 of 0.94 or 1.43 ml., equivalent to 0.143 ml. of acetylene. Since 250 ml. of liquid oxygen are equal to 200,000 ml. of gaseous oxygen, the acetylene content on the gas basis would be 0.7 p.p.m.

Because the depth of color of cuprous acetylide solutions bears a linear relationship to the concentration of acetylene, a deeply colored solution could have been halved or quartered and made up to the original volume and the acetylene multiplied by 2 or 4.

Oks (*3*) uses only one condenser for his work. He claims complete freezing out of the acetylene while maintaining a temperature of −160° C. inside the condenser. The authors found that a sample showed 2.0 p.p.m. of acetylene with one condenser, and 3.3 p.p.m. with two condensers. Another sample showed 2.1 p.p.m. of acetylene with two condensers and only 2.5 p.p.m. with four condensers. The authors concluded that two condensers would be sufficient for all practical purposes. That not all the acetylene is frozen out is due to the vapor pressure of the acetylene even at extremely low temperatures. In addition, the Oks condensers require stopcocks; these are not necessary in the authors' technique.

Weaver (*8*) states that small amounts of carbon dioxide did not affect the colorimetric determination of acetylene, but larger amounts had the same effect as the introduction of a strong electrolyte into the solution. The color of the colloid produced by acetylene carried over in a stream of pure carbon dioxide was too brown to permit any accurate comparison.

A brown scum frequently appeared on the top of the solution in the absorber, but was never strong enough to ruin the test. Apparently this was due to carbon dioxide which would freeze out with the acetylene.

Riese (*5*) states that the stability of Ilosvay's solution is limited, and recommends that the work always be done with freshly prepared solutions. By making up the three components of the Ilosvay solution separately and mixing only when ready for use, as the authors have done, there is always a fresh solution available.

Riese further notes that addition of more ammonia is not to be recommended, since excess ammonia causes the color of the colloid to become more orange in addition to increasing the sensitivity of the solution toward oxygen.

After the authors had used the above method in their laboratory for some time, they supplied the operators in various plants with the equipment shown in Figures 1 and 2, as well as suitable graduates, beakers, and reagent bottles. Since all oxygen plants do not have suitable balances for weighing the solid chemicals, the cuprous chloride was weighed out in 12-gram packages wrapped in paper, and kept in a wide-mouthed bottle. The hydroxylamine hydrochloride was also repackaged into small bottles, so that each bottle was just sufficient for one batch of solution.

A set of instructions for using the equipment and making the test was drawn up and explained to the operators and two or three tests were run through with those expected to continue making the tests. They found no difficulty in running the tests as efficiently as an experienced chemist would have done. During the past year, the authors have been running tests on seven different columns at three different locations and have studied the effects of various factors. The results of tests are summarized below.

Effect of Different Brands of Lubricating Oils. Comparative tests were run, using three different grades of lubricating oil in compressors; a noticeable difference was found in the amount of acetylene accumulated in the column with the different brands of oil.

Effect of Carbide Storage in Air Plants. At the time that daily tests on columns were being run, a broken drum of carbide

Table II. Calibration of No. 348 Corning Filter

(250-cc. sample of liquid oxygen)

Unknown	C_2H_2	Unknown	C_2H_2
Ml.	*P.p.m.*	*Ml.*	*P.p.m.*
100	0.70	50	1.41
90	0.78	40	1.76
80	0.88	30	2.35
70	1.00	20	3.54
60	1.25	10	7.10

Table III. Effect of Carbide Spilled near Plant

Date (1944)	C_2H_2 by Volume Column 1	Column 2
	P.p.m.	*P.p.m.*
1/24	0.25	0.35
1/26	0.75	1.10
1/27[a]	2.60	2.00
1/28	1.50	2.10
1/31	0.90	1.30
2/1	0.60	1.20

[a] Carbide spilled on platform previous night.

was returned by a customer and left on the loading platform overnight. Some of it was spilled on the platform and during the night it rained. Tests on the columns the following day showed its presence, as evidenced by Table III. Column 1 showed the largest increase in these tests, as its air intake was closest to the rising acetylene over the dome of the roof.

Effect of Draining Liquid Oxygen. Strizhevskil (7) states that no method for the safe application of the rectifying apparatus has been found. One method for preventing explosions consists in removal of the liquid from the condenser in which considerable amounts of acetylene accumulate. For this purpose, it is necessary to conduct systematic analyses of the liquid oxygen in the condenser for the presence of acetylene.

Previous to the acetylene testing the authors had been draining and discarding 1 quart of liquid oxygen every 2 hours in the belief that this would reduce the acetylene accumulation in the columns. As daily tests on two 100-meter columns at the same plant gave practically the same results, draining column 2 was discontinued while draining column 1 was continued. The results are tabulated in Table IV.

It was concluded that draining liquid periodically from the main kettle had no effect on the accumulation of acetylene in these columns.

Effect of Moving Air Intake. One column ran much higher in acetylene content than the other columns. Its air intake was in a considerably less advantageous position than the others, in that it was lower and more vulnerable to strange ground currents. Raising the intake obviated this difficulty to a great extent. The average acetylene concentration for the 6 days prior to raising the air intake was 0.8 p.p.m., and for the 9 days after raising the air intake was 0.2 p.p.m.

Effect of Acetylene Plant in the Neighborhood. Tests were made on an oxygen plant located near an acetylene plant which operates intermittently. On days when the acetylene plant was in operation, the tests were noticeably higher than

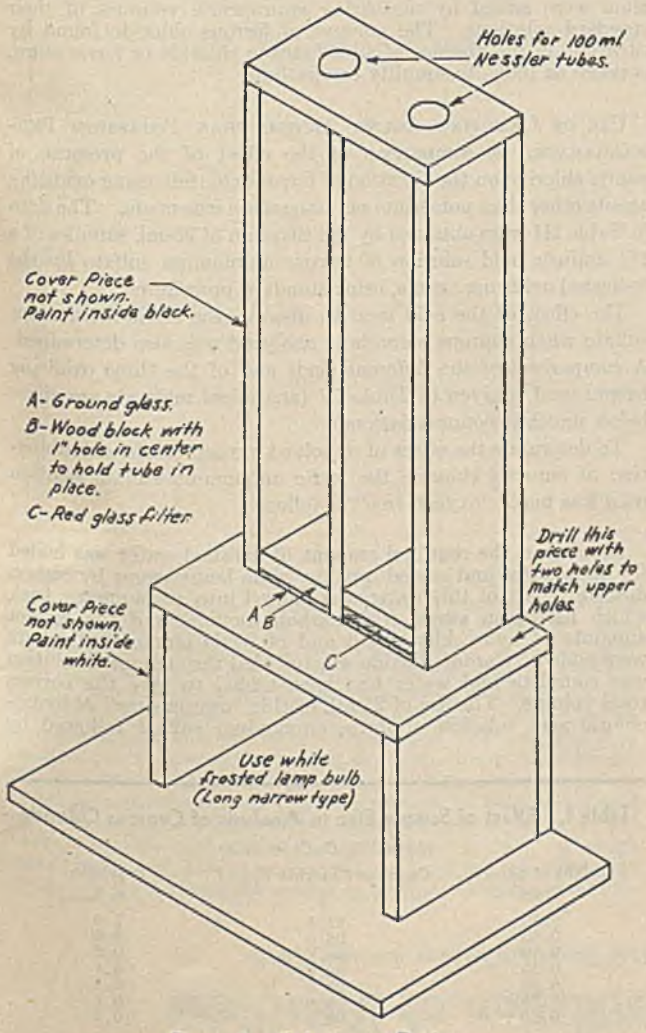

Figure 2. Colorimeter Design

Table IV. Effect of Draining Liquid

Date (1944)	Column 1 Days run since defrosting	Column 1 Test C_2H_2 P.p.m.	Column 2 Days run since defrosting	Column 2 Test C_2H_2 P.p.m.
2/10	19	1.8	1	2.5
2/11	20	0.7	2	0.4
2/12	21	0.2	3	0.0
2/14	1	..	5	0.4
2/15	2	0.5	6	0.5
2/16	3	1.0	7	1.0
2/17	4	1.0	8	0.7
2/18	5	0.5	9	0.5
2/19	6	0.5	10	0.5
2/21	8	0.5	12	0.5
2/22	9	0.6	13	0.5
2/23	10	0.3	14	0.3
2/25	12	0.7	16	0.7
2/26	..	..	17	0.6
2/27	14	0.2	18	0.7
2/28	15	0.7	19	0.7
2/29	16	0.7	20	0.0

Table V. Effect of Acetylene Plant Operating in Neighborhood

Date (1944)	Time	Days Run since Defrosting	C_2H_2, P.P.M.
3/8	11:00 A.M.	3	2.65
3/8	2:00 P.M.	3	0.87[a]
3/8	4:20 P.M.	3	0.70[a]
3/9	6:00 A.M.	4	3.40
3/9	10:35 A.M.	4	1.30[a]
3/9	12:15 P.M.	4	0.70[a]
3/9	2:30 P.M.	4	0.70[a]
3/10	8:00 A.M.	5	2.74
3/10	11:00 A.M.	5	1.25
3/10	2:00 P.M.	5	0.98[b]
3/11	8:00 A.M.	6	5.85[b]
3/11	11:00 A.M.	6	1.35
3/11	12:00 M.	6	1.05[a]
3/11	2:00 P.M.	6	0.75[a]
3/11	6:00 P.M.	6	0.70[a]
3/11	8:00 P.M.	6	0.73[a]
3/11	11:50 P.M.	6	0.95[a]
3/12	8:00 A.M.	7	0.70[a]
3/12	10:00 A.M.	7	0.70[a]
3/12	2:00 P.M.	7	0.70[a]
3/12	6:00 P.M.	7	0.70[a]
3/12	8:30 P.M.	7	0.70[a]
3/12	11:40 P.M.	7	0.60[a]
3/13	10:35 A.M.	8	1.12[c]
3/13	12:45 P.M.	8	0.94
3/13	3:00 P.M.	8	0.90
3/14	2:00 A.M.	9	0.88[a]
3/14	7:00 A.M.	9	0.75[a]
3/14	9:00 A.M.	9	0.70[a]

[a] Acetylene plant not operating.
[b] Liquid drawn every 2 hours between these two tests.
[c] Strong wind blowing away from air intake.

when it was shut down. The prevailing winds blow from the air plant to the acetylene plant and would tend to blow the acetylene away from the plant. There was considerable correlation between wind velocity and the amount of acetylene in the oxygen when the acetylene plant was operating. Extremely high concentrations of acetylene were not found at any time and, although the column ran continuously, it would clean itself out when the acetylene plant was idle.

This self-cleaning of columns is referred to by Burbo (1) and was also noted in the case of the carbide being spilled on the loading platform.

Table V gives sample date from this location. Even when the acetylene plant was operating all day, the first test was invariably higher than the following ones. To check whether or not this was due to the drawing off of liquid, a pint of liquid was drawn off every 2 hours between the last test of March 10 and the first test of March 11. This test was the highest of any reported. Therefore, it is apparent that the draining of liquid does more harm than good.

One explanation for gradual decline of the tests during the day, while the acetylene plant is operating, is that the prevailing winds rise during the day and may blow the acetylene away from the oxygen intake.

CONCLUSIONS

This method involves the use of a glass filter as a permanent color standard. It has been simplified to a point where analyses can be made by nontechnically trained operators. This method is,

under any circumstances, accurate enough to give good comparisons; tests run on seven different columns at three different locations have indicated changes which have led to safer operating conditions.

For more exact work where the absolute value of acetylene is desired, the rubber stoppers and tubing may be replaced with glass and cold filters as described by Shepherd (*6*) used.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of George R. West and the staff of the Stuart Oxygen Co. Research Department who did some of the preliminary work on the method; and of Merle Randall who gave many valuable suggestions. They also wish to acknowledge the work of the operators in the various plants who ran most of the actual tests after the method had been developed.

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Determination of Cuprous Chloride

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DURING recent hydrolysis studies (*5*) it became necessary to determine accurately the purity of solid cuprous chloride and the cuprous chloride content of dilute solutions. As direct titration of cuprous chloride did not give satisfactory results, the indirect method of the AMERICAN CHEMICAL SOCIETY Committee on Analytical Reagents (*1*) was tried. This method lacked both the precision and accuracy required for the analysis of samples of essentially pure solid cuprous chloride. This paper calls attention to the defects of the A.C.S. method and proposes analytical procedures which are more satisfactory for both solid cuprous chloride and its dilute solutions.

EXPERIMENTAL

REAGENTS. Merck reagent grade cuprous chloride was carefully purified by the usual methods (*6*). Determination of chloride ion (by the Volhard method) and of total copper by electrodeposition (after conversion to cupric sulfate) indicated a composition of 99.8% cuprous chloride and 0.2% cupric chloride. The dry cuprous chloride was placed in small glass-stoppered vials and stored in a desiccator over magnesium perchlorate. Cuprous chloride thus prepared and stored showed no change in composition over a period of several months.

All other chemicals used were of reagent grade.

A.C.S. METHOD. Following is the method which is approved by the A.C.S. Committee on Analytical Reagents (*1*) for the determination of cuprous chloride in a solid sample:

Dissolve 0.5 gram in the cold in 25 ml. of ferric ammonium sulfate solution, made by dissolving 10 grams of ferric ammonium sulfate in 100 ml. of dilute hydrochloric acid (1 + 1), add 5 ml. of phosphoric acid, dilute with 200 ml. of water, and titrate with permanganate, correcting for blank on reagents.

Careful application of this method consistently gave low values and poor precision when the sample was essentially 100% cuprous chloride. The degree of error is related to the sample size (Table I).

On the basis of the oxidation-reduction potentials involved, it is expected that complete oxidation of cuprous copper will occur, if a slight excess of ferric iron is present (*4*). Actually, the determination of cuprous chloride by this method is the same as a determination of the equivalent amount of ferrous iron in the presence of the excess ferric iron added and an amount of cupric chloride equivalent to the cuprous chloride of the sample. Factors which would influence the titration are cupric ion, chloride ion, and ferric ion concentration and the nature of the acid medium and of the oxidizing agents.

A study of some of these factors was made by the titration with 0.1 *N* potassium permanganate of 25-ml. samples of a standard solution of ferrous chloride in 1 + 1 hydrochloric acid, in the presence of added cupric chloride and ferric ammonium sulfate as indicated in Table II. Two hundred milliliters of water and 5 ml. of phosphoric acid were used as in the A.C.S. procedure. The added amounts of cupric chloride are the oxidation equivalents of the recorded amounts of cuprous chloride. The indicated amounts of cupric chloride and of ferric alum were added by measuring appropriate volumes of their standard solutions. The amount of ferrous chloride found by titration, in the absence of added cupric chloride or ferric alum, is taken as 100% to simplify comparison.

USE OF OXIDIZING AGENTS OTHER THAN POTASSIUM PERMANGANATE. A comparison of the effect of the presence of cupric chloride on the titration of ferrous chloride using oxidizing agents other than potassium permanganate was made. The data in Table III were obtained by the titration of 25-ml. samples of a 1% sulfuric acid solution of ferrous ammonium sulfate by the indicated oxidizing agents, using standard procedures.

The effect of the acid used to dissolve the ferric ammonium sulfate when cuprous chloride is analyzed was also determined. A comparison of the different acids and of the three oxidizing agents used is given in Table IV (analytical methods are given below under Recommendations).

To determine the effect of dissolved oxygen on the determination of cuprous chloride the ferric ammonium sulfate solution used was made "oxygen-free" as follows:

More than the required amount of distilled water was boiled for 30 minutes and cooled quickly while being swept by carbon dioxide. Part of this water was poured into a volumetric flask which had been swept with carbon dioxide, and the correct amounts of hydrochloric acid and of ferric ammonium sulfate were added. Carbon dioxide was bubbled through until solution was complete and water had been added to give the correct total volume. The use of 25 ml. of this "oxygen-free" *N* hydrochloric acid solution of ferric ammonium sulfate followed by

Table I. Effect of Sample Size in Analysis of Cuprous Chloride

(Actual % CuCl = 99.8)

Weight of Sample	Cuprous Chloride Found	Precision
Gram	%	± %
0.50	97.5	1.0
0.45	98.6	0.2
0.40	98.8	0.2
0.35	98.9	0.1
0.30	98.9	0.1
0.25	98.9	0.1
0.20	98.9	0.1

[1] Present address, Armour Laboratories, Chicago, Ill.

Apparatus for Flash-Distillation of Butadiene

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An apparatus for the flash-distillation of butadiene is described and a diagram shown. Its efficiency has been determined with the aid of the Dorell weathering-test apparatus. Substantially complete removal of butadiene dimer is accomplished without appreciable loss of C_5 hydrocarbons.

IN THE analysis of butadiene, the determination of C_5 hydrocarbons by a Dorell (Dow-Cottrell) weathering tester (*2*) gives high percentages if butadiene dimer is present. Preliminary to the determination it is usually necessary to carry out a flash-distillation of the sample to remove dimer (vinyl cyclohexene) and high-boiling material. Previous methods of doing this have been defective in failing to give a complete removal of dimer without loss of the C_5's which should remain in the volatile fractions. To remedy this difficulty, the apparatus described below has been developed.

APPARATUS

The apparatus (Figure 1) consists of the following parts: *F* is an ampoule forming the kettle of the apparatus. A neck, *G* (15 cm. long), connects the kettle with cup *D*, having an inner cup, *H*. From *H* a closed tube, *T*, extends through the neck and just into the kettle. A cork, *E*, is inserted in the closed tube to keep materials placed in the cup from entering the tube. *C* is a side arm through which the apparatus is filled and emptied. The apparatus is made of Pyrex to lessen the danger of breakage by sudden changes of temperature.

OPERATION

The ampoule is evacuated through *C*, closed off, and the apparatus cooled in a dry ice bath (dry ice in a mixture of chloroform and carbon tetrachloride, 50–50 by weight, *1*). The sample to be flash-distilled is introduced into the cooled, evacuated ampoule. A trap is connected to *C*, evacuated, and closed off at *A*. Cup *H* is filled with a dry ice bath and an excess of dry ice is maintained in the cup throughout the distillation. The trap is opened into the ampoule, the bath is removed from around it, and the trap is placed therein. Caution should be used to keep out all air or noncondensable gases at dry ice bath temperature. Material that does not condense will prevent the distillation of the butadiene, since the distillation is carried out in a closed system. The dry ice bath in the cup maintains a reflux of butadiene separating the dimer and high-boiling material from the butadiene and C_5's. If the cork is not in the tube, a heavier reflux is caused, requiring a longer time for distillation; with the cork in place about an hour is required. When the ampoule has come to room temperature, the trap is closed at *B* and the sample is ready

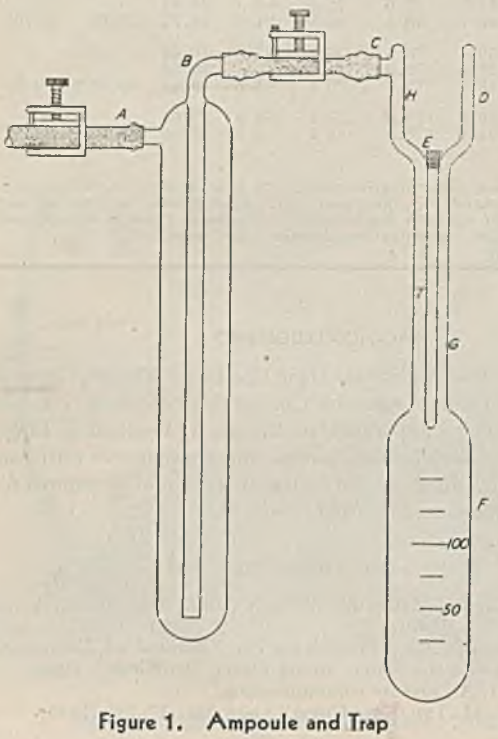

Figure 1. Ampoule and Trap

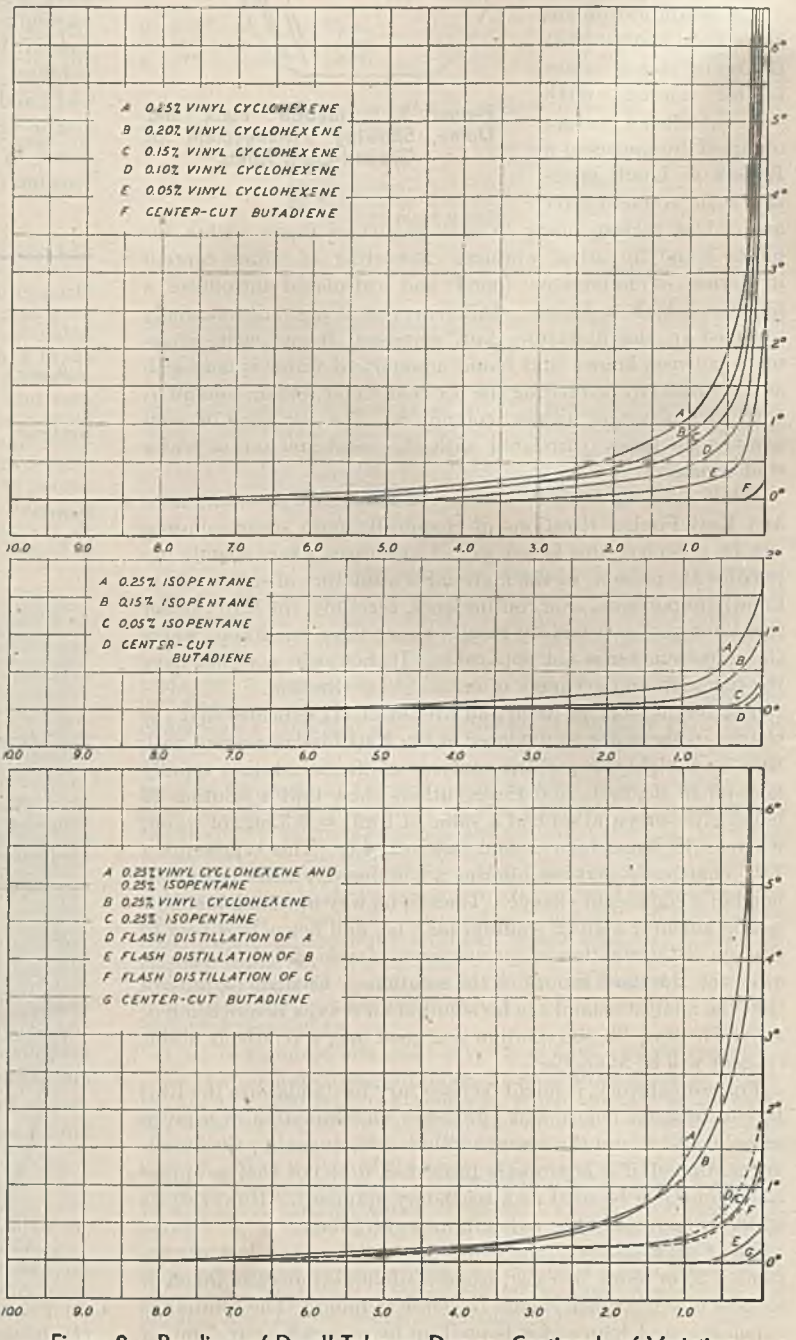

Figure 2. Readings of Dorell Tube vs. Degrees Centigrade of Variation

equal to 1 ml. of Karl Fischer reagent, and (2) the number of milligrams of water in each milliliter of alcohol used in the back-titrations.

The sample of sirup is treated exactly like the water used in the standardization of the solutions. Three to five coarse drops, depending on the water content, are carefully weighed out and added to 20 to 25 ml. of the Karl Fischer reagent, and immediately back-titrated with the standard methanol. A sample series of determinations is shown in Tables I and II.

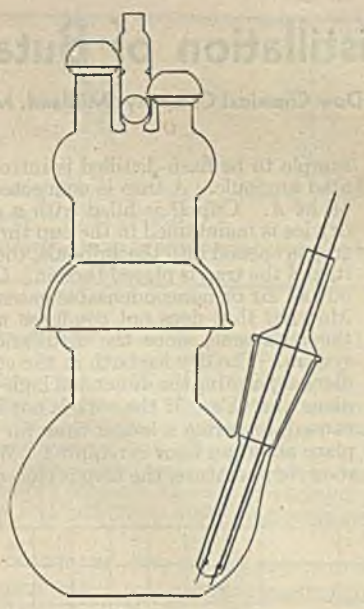

Figure 2. Titration Flask and Dome, Showing Arrangement of Ground-Glass Joints

An examination of the data shows that the milligrams of water found check with the calculated values obtained by means of a Bausch & Lomb precision sugar refractometer and tables corresponding to each particular sugar, within the limits found by other workers. Reporting of water content in terms of milligrams found and calculated introduces a fallacious, high precision. Differences of 2 mg. are commonly reported in the literature, but, expressed in per cent, agreement between known and found amounts of water is not ideal, as is revealed by comparing the per cent water found, column 7, with the observed values, column 8. The per cent discrepancy is obviously correlated with the total amount of water that is present.

While close agreement between refractometric determinations and Karl Fischer titrations of chemically pure sugar solutions can be expected, this is not so in those cases where soluble impurities are present, or the material is a mixture of sugars of unknown proportions. For routine work, certainly, the Karl Fischer titrations give satisfactory results under those conditions where the refractometer is not applicable. It, however, does not have the precision and accuracy of an acid-base titration.

The recent work of Aepli and McCarter (*1*) indicates that the change in the water equivalence of the Karl Fischer reagent with time is a highly important matter. A fresh solution rapidly falls off in strength, and these authors show that a solution 22 hours after preparation had a value of 1 ml. = 5.3 mg. of water, whereas 18 hours later it had fallen to 4.6. This represents a 14% change, so that even during a working day there is a likelihood of a significant change. There is no way of telling just how temperamental a given solution may be, and hence it is best to make a determination of an unknown sample shortly before or after the standardizations of the solutions. Frediani (*3*) advises that the analyst should age his solution for a week before using it, at which time, "if the solution is a good one, a relatively stable reagent will be available".

For critical work, it might be necessary to standardize the Karl Fischer reagent before and after each determination of a given sample, and to use the average values. Fortunately, the standard methanol, if it is properly protected, does not change appreciably and can be used as a secondary standard. However, its water content should be redetermined every day.

The Karl Fischer method, when used with sugar solutions containing 20 or more % water, has certain limitations and inherent sources of error which should be borne in mind. The solution is expensive, and 1 liter of it is used up by approximately 5 ml. of water. The reagent has a rather high viscosity, and buret drainage therefore becomes a serious factor. To overcome these difficulties, the reagent might better be diluted with a mixture of absolute methanol–pyridine (3 to 1), so that its water equivalence is between 2 and 3 mg. per ml. High-grade pyridine must be used to assure stability. It is obvious that a buret reading must be at least 15 to 20 ml. before calibration errors in an uncalibrated buret, and the drainage and reading errors become sufficiently small relative to the total volume used, not to introduce too large percentage errors. Furthermore, the reagent decomposes on standing and produces an oily film in the buret. It is therefore convenient to have two Karl Fischer reagent burets available, so that a clean and dry one is ready at the beginning of each day.

Samples of sugar solutions containing large amounts of water force one of three choices: (1) a small sample weighing 60 to 70 mg., for the sake of economy, (2) a sample two or three times that amount in order to enable more precise weighings, or (3) a large sample, diluting with absolutely anhydrous methanol and taking an aliquot. The first choice is not desirable in ordinary work because it would require calibrated weights, or the use of a microbalance. Choice 3 introduces the problem of preparing, storing, and handling an anhydrous hygroscopic liquid.

The work is being continued with commercial sirups and molasses in an endeavor to determine the relationship between vacuum drying of samples and the Karl Fischer titration.

Table II. Analyses of Sugar Solutions[a]

1 Sugar	2 Weight	3 H_2O Found	4 H_2O Calcd.	5 Difference	6 H_2O Found	7 Av.	8 H_2O, Refractometer
	Gram	*Mg.*	*Mg.*	*Mg.*	%	%	%
Dextrose	0.1152	68.1	69.2	−1.1	59.13		
	0.1119	65.9	67.3	−1.4	58.92	59.03	60.11
	0.0901	53.8	53.7	+0.1	59.72		
	0.1441	86.1	85.8	+0.3	59.74	59.73	59.57
Sucrose	0.1941	67.0	67.1	−0.1	34.53		
	0.2036	71.1	70.4	+0.7	34.92		
	0.1845	63.0	63.8	−0.8	34.13	34.73	34.59
	0.2172	74.9	75.5	−0.6	34.48		
	0.3020	107.2	105.0	+2.2	35.50		
	0.3546	121.8	123.3	−1.5	34.35	34.78	34.77
	0.4438	109.0	107.4	+1.6	24.56		
	0.3123	77.0	75.6	+1.4	24.65		
	0.3577	88.4	86.6	+1.8	24.73	24.65	24.21
Levulose	0.3931	76.5	78.3	−1.8	19.44		
	0.3715	73.6	74.0	−0.4	19.82		
	0.3847	75.0	76.6	−1.6	19.51	19.59	19.92
Commercial invert sirup	0.2678	77.0	76.1	+0.9	29.03		
	0.2419	70.1	68.2	+1.9	28.99	29.01	28.42

[a] Representative determinations made on five different days, involving completely new standardizations each day. Karl Fischer reagents of fourfold variations in strength are included. However, there is no apparent correlation between concentration of reagent and precision.

ACKNOWLEDGMENTS

The writers wish to express their thanks to William Geyer of the Scientific Glass Apparatus Co. for his cooperation in the manufacture of the apparatus, to Harold A. Frediani of Eimer and Amend for his generous advice and constructive criticism, and to Frederick Bates of the National Bureau of Standards for kindly supplying a sample of pure levulose.

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Determination of Moisture in Sugar Solutions with the Karl Fischer Reagent

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Apparatus and procedure are described for determining moisture in sugar solutions with the Karl Fischer reagent. Data on representative analyses are given, with comparisons between refractometric determinations and Karl Fischer titrations.

THE Karl Fischer reagent has come into wide use for the quantitative determination of water in a variety of products. In a recent article, Johnson (*4*) gives an extensive bibliography.

This reagent, which is commercially available (*2*), consists of a solution of iodine and sulfur dioxide in a mixture of anhydrous methanol and pyridine. It is extremely sensitive to atmospheric moisture, and consequently titrations with it must be carried out in a completely closed system, especially where minute quantities of water are being determined. Furthermore, the necessity for stirring the reaction mixture during the titration introduces an extra difficulty into the design of a suitable apparatus.

The equipment described below is rugged and overcomes all the manipulative difficulties.

APPARATUS

Two 50-ml. automatic burets (Scientific Glass Apparatus Co. J-740) are so modified that the lower ends of the barrels of the Fresenius stopcocks are enlarged and formed into the outer parts of semiball 18/9 joints (Figure 1). The titration vessel (Figure 2) is a flat-bottomed extraction flask of 250-ml. capacity provided with a mouth, which is a male semiball 65/40 joint, and a ₹14/35 side tube through which go the mutually insulated platinum electrodes sealed into a tube with a male ₹14/35 joint and connected to the brush posts of the titrimeter. The flask is covered with a bell-shaped dome, the lower part of which is a female semiball 65/40 joint. From the top of the dome project two male semiball 18/9 joints set at sufficiently differing heights to permit free rotation of the buret stopcocks. In addition, the dome is provided with a check valve (Scientific Glass Apparatus Co. J-4880 B) to permit venting of the apparatus whenever liquid is being admitted into the flask from the burets. The male 18/9 joints fit into the burets which are provided with stopcock plugs with tips 16.5 cm. long.

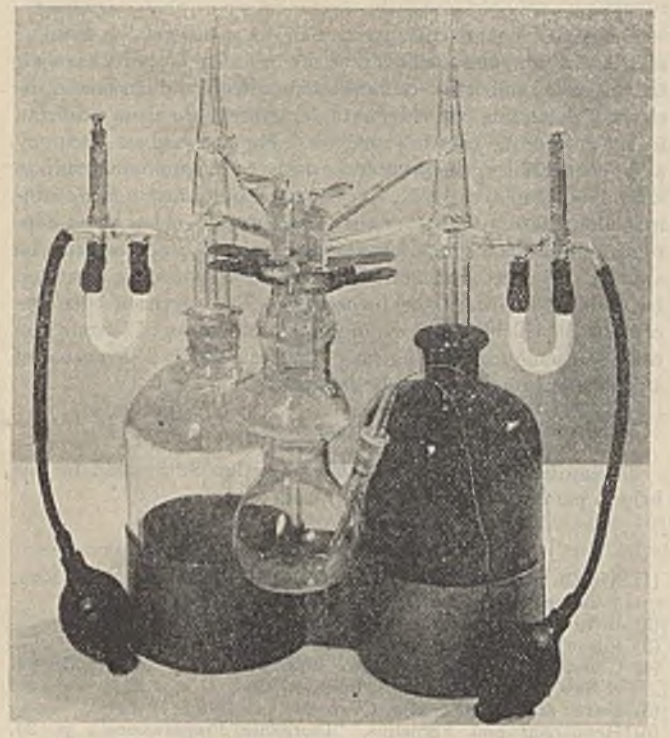

Figure 1. Glass Assembly of Titration Apparatus

Stirring is accomplished by means of a piece of iron bolt 2.81 cm. (1.125 inches) long and 0.47 cm. ($^3/_{16}$ inch) in diameter, fitting snugly and sealed into a piece of Pyrex tubing, the center of which has been blown out into a small bulb. An Alnico horseshoe magnet (Fisher Scientific Co. 12-012), mounted on a motor provided with a rheostat, is placed under the flask.

Table I. Standardizations of the Solutions

Standard Methanol *vs.* Karl Fisher Reagent

K.F. Reagent	Standard Methanol	1 Ml. of Alcohol ≏ *a* Ml. of K.F.
Ml.	*Ml.*	
13.45	40.70	0.3305
13.90	42.20	0.3294
13.60	41.05	0.3313
		Av. 0.3304

Titration of Known Weights of Water

Water	K.F. Reagent	Standard Methanol Back-Titration	Ml. of K.F. ≏ to Standard Methanol	Net K.F.	1 Ml. of K.F. ≏ Gram of Water
Gram	*Ml.*			*Ml.*	
0.1020	26.90	3.50	1.16	25.74	0.003963
0.1145	29.75	2.50	0.83	28.92	0.003959
0.1241	31.95	2.30	0.76	31.19	0.003979
					Av. 0.003967

Water Equivalent of Standard Methanol

Ml.	K.F. Ml.		Gram water/ml. methanol
40.70	≏ 13.45	× 0.003967 =	0.001311
42.20	≏ 13.90	× 0.003967 =	0.001307
41.05	≏ 13.60	× 0.003967 =	0.001314
			Av. 0.001311

PROCEDURE

In operation, the apparatus is assembled, and a measured amount of Karl Fischer reagent is run into the flask. The stirrer is started, and standard methanol is rapidly added from the other buret until the solution, which originally had the appearance of tincture of iodine, turns to a light, reddish brown. The methanol is then added slowly, and finally dropwise until the end point is reached. With the Fisher Scientific Co.'s titrimeter employing a polarized platinum-platinum electrode pair, this is indicated by the closing of the "magic eye" (*2*). Fresh Karl Fischer reagent turns to a chromate yellow, but an old solution remains brownish at the end point, making it more difficult to gage visually the final stage of the titration. For maximum sensitivity, it is important that the platinum wires be perfectly clean, and it is advisable to bathe them for an hour or two in strong, hot dichromate–sulfuric acid cleaning solution.

It was found that the absolute methanol sold by the Carbide and Carbon Chemicals Corporation contains approximately 0.0013 gram of water per milliliter, which makes it excellently suitable to use for back-titrations, because it is roughly only one fourth as strong as the average Karl Fischer reagent. Three or four determinations are made in this manner, and the average value is expressed as:

1 ml. of standard methanol ≏ *a* ml. of Karl Fischer reagent

Next, from a small weight pipet, 2 coarse drops of water, weighing about 0.1200 gram, are removed, added directly to 25 ml. of Karl Fischer reagent in the flask, and immediately back-titrated with the standard methanol. The burets are read to the nearest 0.01 ml. The weight of the water is noted accurately to 0.1 mg. A 15-ml. Erlenmeyer flask with ₹19/10 outside grind, provided with a cover through which is sealed a medicine dropper, and fitted with a small rubber bulb, is recommended for weighing out the water, as well as samples of sirup. A minimum of three such samples of water are weighed out, and back-titrated with the standard methanol. From this information, coupled with the alcohol–Karl Fischer reagent equivalence previously determined, it is possible to calculate: (1) the number of milligrams of water

Table II. Effect of Cupric Chloride and Ferric Alum on Titration of Ferrous Chloride by Permanganate

Run	CuCl Equivalent to Added $CuCl_2$	Ferric Alum Added	Ferrous Chloride Found
	Gram	*Gram*	%
A	0.00	0.0	100.0
B	0.25	0.0	94.7
C	0.25	1.0	98.7
D	0.50	0.0	93.9
E	0.50	1.0	98.7
F	1.00	0.0	93.4
G	1.00	1.0	98.2

Table III. Effect of Cupric Chloride upon Titration of a 1% Sulfuric Acid Solution of Ferrous Ammonium Sulfate

CuCl Equivalent to Added $CuCl_2$	Ferrous Chloride Found		
	$KMnO_4$	$K_2Cr_2O_7$	$Ce(SO_4)_2$
Gram	%	%	%
0.00	100.0	100.0	100.0
0.25	96.9	99.7	99.8
0.50	95.3	99.5	99.8

titration with potassium dichromate gave 99.5% cuprous chloride as compared with 99.2% of a similar solution, made in contact with air was used.

DISCUSSION

The poor results obtained in the analysis of 0.5-gram samples of cuprous chloride by the A.C.S. method may be caused by an insufficient amount of ferric ammonium sulfate solution for the oxidation of the cuprous copper. From the specification "25 ml. of ferric ammonium sulfate solution, made by dissolving 10 grams of ferric ammonium sulfate in 100 ml. of dilute hydrochloric acid" it is assumed that the intention is to use 2.5 grams of ferric ammonium sulfate. This would allow a slight excess of oxidizing agent, since 0.5 gram of cuprous chloride is equivalent to 2.44 grams of ferric alum. However, the addition of 100 grams of ferric ammonium sulfate to 1000 ml. of 1 + 1 hydrochloric acid, in a constant-temperature bath at 30° resulted in 1060 ml. of solution, containing only 2.36 grams of ferric ammonium sulfate per 25 ml. Thus, part of the cuprous chloride is oxidized by ferric iron, part by permanganate, and an indefinite amount by atmospheric and dissolved oxygen (*3*), the latter amount being proportional to time and to the amount of agitation (*2*). For 0.5-gram samples of essentially pure cuprous chloride, the permanganate concentration should be slightly more than 0.1 *N*, since 0.5 gram of cuprous chloride is equivalent to more than 50 ml. of 0.1 *N* solution. Table II indicates that the adverse effects of cupric ion are partially, but not entirely, offset by the presence of the ferric alum.

Comparison of runs A, B, and D of Table II with the data in Table III indicates that the effect of cupric chloride upon the permanganate titration of ferrous iron is lessened by decreased chloride ion concentration and that the effect of cupric chloride is less when potassium dichromate or ceric ammonium sulfate is used.

RECOMMENDATIONS

The following three methods for the determination of the cuprous chloride content of solid cuprous chloride have all proved superior to that recommended by the A.C.S. Committee on Analytical Reagents:

Potassium Permanganate. Weigh 0.3 gram of cuprous chloride into a dry 500-ml. Erlenmeyer flask, add 25 ml. of ferric ammonium sulfate solution, made by dissolving 10 grams of ferric ammonium sulfate in sufficient 3 *M* sulfuric acid to make 100 ml., and swirl gently until dissolved. Add 200 ml. of water and 5 ml. of phosphoric acid, and titrate with 0.1 *N* permanganate to the first pink color which persists for 15 seconds. A blank must be run on the reagents.

Potassium Dichromate. Weigh 0.3 gram of cuprous chloride into a dry 500-ml. Erlenmeyer flask, add 25 ml. of ferric ammonium sulfate solution, made by dissolving 10 grams of ferric ammonium sulfate in sufficient *N* hydrochloric acid to make 100 ml., and swirl gently until dissolved. Add 300 ml. of a solution containing 80 ml. of sulfuric acid and 25 ml. of phosphoric acid per liter, add 5 drops of 0.2% barium diphenylaminesulfonate indicator solution, and titrate with 0.1 *N* dichromate to the first permanent purplish tinge. A blank must be run on the reagents.

Ceric Ammonium Sulfate. Weigh 0.3 gram of cuprous chloride into a dry 500-ml. Erlenmeyer flask, add 25 ml. of ferric ammonium sulfate solution, made by dissolving 10 grams of ferric ammonium sulfate in sufficient 3 *M* sulfuric acid to make 100 ml., and swirl gently until dissolved. Add one drop of ferrous-phenanthroline indicator solution and titrate with 0.1 *N* ceric ammonium sulfate solution (made up in 0.5 *M* sulfuric acid solution). A blank must be run on the reagents.

For determination of the cuprous copper content of dilute solutions the following procedure is recommended:

Pipet 25 ml. of the cuprous copper solution into 25 ml. of ferric ammonium sulfate solution, made by dissolving 33 grams of ferric ammonium sulfate in sufficient 3 *M* sulfuric acid to make 1000 ml. Add 250 ml. of water and 1 drop of ferrous-phenanthroline complex indicator solution, and titrate with 0.1 *N* ceric ammonium sulfate solution (made up in 0.5 *M* sulfuric acid). A blank must be run on the reagents.

This quantity of ferric iron is sufficient for solutions containing up to 0.6% cuprous chloride.

For applications which do not require the highest accuracy, the dichromate procedure for solid cuprous chloride is suggested. (For analysis of dilute solutions, a modification similar to that given for ceric ammonium sulfate may be used.) The *N* hydrochloric acid solution of ferric alum has the advantage of dissolving the cuprous chloride in only a few seconds.

Table IV. Effect of Acid Used in Ferric Ammonium Sulfate Solution

Acid Used as Ferric Alum Solvent[a]	Cuprous Chloride Found		
	$KMnO_4$	$K_2Cr_2O_7$	$Ce(SO_4)_2$
	%	%	%
N HCl	99.4	99.2[b]	99.6
6 *N* HCl	98.9	98.7	99.2
0.5 *M* H_2SO_4	99.3	99.2	99.6
3 *M* H_2SO_4	99.7	99.4	99.8[c]

[a] Solutions prepared in contact with air.
[b] Oxygen-free value = 99.5.
[c] Purity by electrodeposition = 99.8.

The stability and transparency of its solutions, its ease of standardization, and the high precision resulting from its use with the suggested indicator recommended potassium dichromate, instead of potassium permanganate, for general use as an oxidizing agent in cuprous chloride analysis. For the highest accuracy and dependability, the procedures using ceric ammonium sulfate should be employed, with oxygen-free solutions of ferric ammonium sulfate. Whatever the procedure, the chloride ion concentration should be kept low and an excess of ferric iron must be assured. It is recommended that the amount of ferric iron used be at least 1.5 times the theoretical. The precision then becomes that which is attained in the determination of ferrous iron using the same oxidizing agent. The accuracy to be expected of a particular procedure may be estimated from Table IV.

ACKNOWLEDGMENT

The authors would like to thank Gordon Sutherland for his help in part of the experimental work.

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Table I. Temperature Readings

Residual Volume Ml.	Temperature ° C.	Temperature Difference ° C.
10.0	−4.5	...
9.0	−4.7	...
8.0	−4.7	0.0
7.0	−4.7	0.0
6.0	−4.7	0.0
5.0	−4.7	0.0
4.0	−4.7	0.0
3.0	−4.7	0.0
2.5	−4.7	0.0
2.0	−4.6	0.1
1.5	−4.6	0.1
1.0	−4.6	0.1
0.8	−4.6	0.1
0.6	−4.6	0.1
0.4	−4.6	0.1
0.2	−4.5	0.2
0.1	−4.5	0.2
Pump stops	−4.4	0.3
Dry point	−4.3	0.4

for C_5 determination or any other determination requiring a flash-distilled sample.

DISCUSSION

In order to test the efficiency of the apparatus, butadiene samples have been submitted to flash-distillation and then analyzed in the Dorell weathering-test apparatus. For the determination of C_5 hydrocarbons, 40 ml. of distilled sample are placed in the boiler of the Dorell and 30 ml. are allowed to "weather away" before the heat is turned on and temperature readings are taken. These readings are taken at 10.0, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0, 0.8, 0.6, 0.4, 0.2, and 0.1 ml., and when the pump stops and the boiler becomes dry. A typical record is given in Table I.

The differences starting at 8.0 ml. between the initial and succeeding temperatures observed are plotted. This curve is compared with curves obtained by plotting the temperature differences of butadiene using known amounts of isopentane run in the same way. Temperature readings at 10.0 and 9.0 ml. are disregarded because the thermometer is still in the liquid phase only and will not give a true boiling point.

Figure 2 (upper) shows the curves produced by center-cut butadiene with varying amounts of butadiene dimer added. Curve *F* is made by plotting temperature differences of center-cut butadiene. It gives almost a straight line, as would be expected. There are significant differences between the curves obtained with varying amounts of dimer.

Figure 2 (center) shows butadiene with different amounts of isopentane. In Figure 2 (lower) are plotted curves obtained with the following mixtures:

A. Butadiene with 0.25% dimer and 0.25% isopentane, not flash-distilled.
B. Butadiene with 0.25% dimer, not flash-distilled.
C. Butadiene with 0.25% isopentane, not flash-distilled.
D. Curve after flash-distillation of *A*.
E. Curve after flash-distillation of *B*.
F. Curve after flash-distillation of *C*.
G. Curve of center-cut butadiene.

Curve *D* shows the almost complete removal of dimer and the retention of C_5's with the butadiene. Curve *E* is representative of the removal of dimer with no C_5's present. The amount of dimer left after flash-distillation with this apparatus expressed as C_5's would be approximately 0.05% which is very small. Curve *F* shows the effect of the flash-distillation on C_5's.

Although the flash-distillation apparatus described was designed specifically for removing dimer and other high-boiling materials from butadiene containing C_5's, it is believed to offer possibilities for other separations. Reflux ratios might be changed by the use of different cooling media or by allowing tube *T* to be filled with coolant.

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Simple Hydrostatic Gravitometer

For Rapid Determination of the Specific Gravity of Liquids

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An apparatus is described for the rapid, precise determination of the specific gravity of selected liquids. Its use is based upon the principle that the change in height of two columns of liquids exposed to the same change in vacuum (or pressure) is inversely proportional to the specific gravity. When one liquid is of known specific gravity, the specific gravity of the other may be calculated. The apparatus is simple, easily constructed, and inexpensive, and is particularly suitable for determining the specific gravity of a large number of similar samples in control testing. The standard deviation of a single value from the value obtained by pycnometer is $\pm 1.4 \times 10^{-4}$ specific gravity unit. The speed with which the determination may be made makes it practical to improve this agreement by calculating the average of a number of determinations on a single sample.

IT IS a well-known principle of hydrostatics that the heights to which two columns of liquids of different specific gravities will rise when exposed to the same vacuum are inversely proportional to their specific gravities. This principle has been applied to the measurement of specific gravities.

Ciochina (*1*) described an apparatus for this purpose which consisted of two U-tubes placed side by side, with a millimeter scale between two of the arms—one from each U-tube—and with those arms joined. By means of a system of stopcocks water is placed in one U-tube and the sample in the other. The levels are read on the millimeter scale, pressure or vacuum is applied through the joined arms, and the levels are read again. From the change in levels and the known specific gravity of the standard liquid (water), the specific gravity of the liquid to be measured may be calculated by a simple inverse proportion. Accuracy to within a few units in the fourth decimal place was reported, but the authors were not able to confirm this. Some of the difficulty may have been caused by the stopcocks which are part of this apparatus. Another disadvantage of this apparatus is that it is necessary (according to Ciochina) to use a vernier in order to get the precision reported.

Another apparatus based on the same hydrostatic principle has been proposed by Davidson and co-workers (*2*, *3*). The liquid under examination is placed in a Z-tube, so that its height is fixed, and the standard liquid is placed in an L-tube manometer. By proper graduation of a scale fixed to the L-tube, the specific gravity of the liquid in the Z-tube may be read. A precision of from 0.1 to 0.2% is claimed (in other words the specific gravities are readable only to the third decimal place). This apparatus is constructed for use with small volumes of liquid.

Frivold (*5*) described an apparatus, which was claimed to be precise to $\pm 10^{-7}$, but it is too complicated for rapid routine use.

This paper describes an apparatus which is based on the same hydrostatic principle as those just mentioned, but has certain ad-

vantages over them. The apparatus may be constructed in a short time from simple equipment found in most laboratories. There are no essential stopcocks which can get out of order, and it gives specific gravities which are comparable in accuracy to those obtained by a pycnometer under ordinary conditions of control work. The apparatus is most suitable for rapid control work where specific gravities must be determined for a large number of samples of selected liquids of similar composition. Accurate values should be obtainable by workers of insufficient skill to be trusted with pycnometers, Westphal balances, or high precision hydrometers. Although no work was done with samples of limited volume, an extension of the method to such samples is conceivable.

Figure 1

APPARATUS

The apparatus (Figure 1) consists of two 150-cm. (5-foot) lengths of glass tubing of as nearly equal inside diameter as can be found (both 3- and 6-mm. inside diameter tubings have been used), fixed on either side of a meter rule, joined at the top to a Y-tube by tightly fitting rubber connections, and bent, as shown, at the bottom. The Y-tube is attached to a source of vacuum which can be regulated or released by means of a screw clamp and a stopcock attached to a rubber tube. Both the upper and the lower 10 cm. of the glass tubing and the meter rule must be left unobstructed in order to enable readings to be made. The lower ends of the apparatus dip into 50- or 100-ml. beakers chosen to be as nearly alike as possible in diameter. One beaker is for the sample, the other for the standard liquid. The apparatus must be kept scrupulously clean and must be placed where there are no drafts or sudden changes in temperature.

PROCEDURE

One side of the apparatus is rinsed with the liquid to be examined and the other side with the standard liquid. The standard liquid is preferably of similar composition to the sample; in fact, it may under some circumstances very well be part of an actual batch of the type of liquid to be controlled whose specific gravity has been carefully determined by pycnometer or Westphal balance. The beakers are filled to about two thirds of their capacity with their respective liquids, keeping the final level well below the flare of the beaker. The tubes are immersed to within about 1 cm. of the bottoms of the beakers. By a gradual application of vacuum the liquid columns are raised nearly to the top of the scale, the stopcock is closed, and readings are made of the positions of the two menisci (estimating to the smallest possible fraction of a millimeter). The two readings should be made as close together in time as possible, so that there will be no changes in the positions of the menisci while the readings are being made. Subsequent changes are of no effect. The vacuum is then released slowly, to allow for drainage as the columns drop, and when the menisci are at about 5 cm., the stopcock is again closed and readings are repeated.

For extremely volatile liquids with which a vacuum might be undesirable, pressure could be used, by having the sample and standard in closed flasks attached to a common source of pressure. The changes in technique that might be required should be obvious. This modification might also be desirable for very hygroscopic liquids, in which case it would be possible to protect the liquids against access of atmospheric moisture by drying tubes.

CALCULATIONS

General Method. Let hsa and hst equal the readings for sample liquid and standard liquid, respectively, at the top of the columns, in cm.

$h'sa$ and $h'st$ = the corresponding readings at the bottom of the columns, in cm.

Sst = the specific gravity of the standard at t/t'

Ssa uncorrected = the specific gravity of the sample at t/t'

$hst - h'st = A$ and $hsa - h'sa = B$

Then
$$Ssa \text{ uncorrected} = Sst\ A/B \quad (1)$$

To Ssa uncorrected there must be added or subtracted a small "asymmetry correction" for the apparatus, which is discussed below.

Approximate Method. For many purposes a less exact but more rapid method of calculation may be used. By this method

$$Ssa \text{ uncorrected} \cong Sst + 0.01\ (A - B) \quad (2)$$

This method of calculation, although merely an approximation, will give values which are fairly close to the true value, provided the term $(A - B)$ is small and provided 100 Sst is not much different from B.

The correct increment to be added to Sst to obtain Ssa may be calculated from Equation 1 in terms of $A - B$ and B (rather than by calculating Ssa from the ratio A/B) by substituting for A/B the equivalent term $1 + (A - B/B)$. (The latter is obtained from A/B by adding $B - B$ to the numerator.) Equation 1 then becomes

$$Ssa \text{ uncorrected} = Sst\ [1 + A - B/B)] = Sst + Sst\ (A - B/B)$$

or

$$Ssa \text{ uncorrected} - Sst = Sst\ (A - B/B) \quad (3)$$

Table I gives a comparison of the values of the increments calculated for benzene (Sst = 0.88) by means of both Equations 3 and 2. From this it may be seen that under appropriate conditions even the approximate method of calculation leads to only small errors.

Nomographs. Nomographs may be constructed to avoid most of the calculations, but in order to get readings to the fourth decimal place, the nomographs would have to be restricted to narrow specific gravity ranges.

Table I. Comparison of Increments Calculated by Exact and Approximate Methods

Assumed Value A−B	Assumed Value B	Increment to Be Added to Sst[a]: Exact calculation by Equation 3	Increment to Be Added to Sst[a]: Approximate calculation by Equation 2
Cm.	*Cm.*		
0.50	88	0.0050	0.0050
0.50	92	0.0048	0.0050
0.50	84	0.0052	0.0050
0.30	88	0.0030	0.0030
0.30	92	0.0029	0.0030
0.30	84	0.0031	0.0030
0.10	88	0.0010	0.0010
0.10	92	0.0010	0.0010
0.10	84	0.0010	0.0010

[a] When $A - B$ is positive, the exact or the approximate increment will be positive; when $A - B$ is negative, they will be negative.

Table II. Specific Gravity Determinations

Sample No.	Specific Gravity, 15.5° C./15.5° C.: By pycnometer	By hydrostatic method	Hydrostatic Average Minus Pycnometer Value × 10^4
Benzene			
1	..	0.8835, 0.8835, 0.8835, 0.8834, Av. 0.8835	...
2	..	0.8822, 0.8823, 0.8823, 0.8822, Av. 0.8823	...
3	..	0.8823, 0.8822, 0.8823, 0.8824, Av. 0.8823	...
4	..	0.8837, 0.8835, 0.8836, 0.8836, Av. 0.8836	...
5	..	0.8825, 0.8824, 0.8825, 0.8824, Av. 0.8825	...
6	..	0.8823, 0.8822, 0.8823, 0.8823, Av. 0.8823	...
Toluene			
1	0.8707	0.8708, 0.8709, 0.8708, 0.8710, Av. 0.8709	+2
2	0.8707	0.9708, 0.8708, 0.8708, 0.8710, Av. 0.8709	+2
3	0.8705	0.8706, 0.8705, 0.8706, 0.8705, Av. 0.8706	+1
4	0.8708	0.8708, 0.8708, 0.8709, 0.8710, Av. 0.8709	+1
5	0.8706	0.8706, 0.8707, 0.8709, 0.8708, Av. 0.8708	+2
6	0.8708	0.8708, 0.8708, 0.8708, 0.8708, Av. 0.8708	0
Xylene			
1	0.8678	0.8677, 0.8678, 0.8677, 0.8676, Av. 0.8677	−1
2	0.8677	0.8675, 0.8676, 0.8673, 0.8674, Av. 0.8675	−2
3	0.8687	0.8687, 0.8688, 0.8688, 0.8686, Av. 0.8687	0
4	0.8686	0.8683, 0.8684, 0.8686, 0.8685, Av. 0.8685	−1

Table III. Specific Gravity Determinations

Sample	Specific Gravity 25°/25° C. By pycnometer	By hydrostatic method	Hydrostatic Average Minus Pycnometer Average × 10^4
1. *m*- and *p*-cresols	1.0325, 1.0324 Av. 1.0325	1.0324, 1.0326, 1.0326 1.0325	0
2. *m*- and *p*-cresols and xylenol intermediate	1.0285, 1.0285 Av. 1.0285	1.0285, 1.0285, 1.0286 1.0285	0
3. *o*-, *m*-, and *p*-cresols intermediate	1.0355, 1.0355 Av. 1.0355	1.0354, 1.0354, 1.0356 1.0355	0
4. Phenol, *o*-cresol intermediate	1.0626, 1.0625 Av. 1.0626	1.0627, 1.0627, 1.0627, 1.0626 1.0627	+1
5. *o*-Cresol	1.0431, 1.0430 Av. 1.0431	1.0431, 1.0431, 1.0431, 1.0430 1.0431	0
6. *o*-, *m*-, and *p*-cresols intermediate	1.0358, 1.0357 Av. 1.0358	1.0356, 1.0358, 1.0360, 1.0360 1.0359	+1
7. *m*- and *p*-cresols	1.0326, 1.0325 Av. 1.0326	1.0323, 1.0325, 1.0325, 1.0325 1.0326 1.0325	−1
8. Phenol, *o*-cresol intermediate	1.0605, 1.0605 Av. 1.0605	1.0603, 1.0603, 1.0603, 1.0603 1.0603	−2

CALIBRATION OF APPARATUS AND ASYMMETRY CORRECTION

Differences that may exist in the bores of the tubes and beakers for the sample and the standard will introduce a systematic error which should be determined for the apparatus under the same conditions as will actually apply in use, and with the same type of sample. The apparatus is calibrated by placing the same liquid on both sides and determining the value A/B, considering the liquid on that side of the apparatus corresponding to A as the standard and that on the other side as the sample. The "asymmetry" correction to be applied to *Ssa* uncorrected is then *Ssa* uncorrected (1.0000 − A/B). If, in actual determinations, the sample and the standard are measured on the same side of the apparatus as corresponds to the side for B and A, respectively, then the sign of the correction as calculated will be valid. The correction should be reproducible and should affect only the fourth decimal place.

RESULTS

Table II gives the results of specific gravity determinations of benzene, toluene, and xylene by pycnometer and by the hydrostatic method. In each case a sample of the same substance was used as a standard—i.e., benzene, toluene, and xylene were used as standards for benzene, toluene, and xylene, respectively. If any one of these was used as a standard for the other, errors in the third decimal place were produced.

Table III gives the results of specific gravity determinations of a number of cuts obtained in the distillation of tar acids, using No. 5 as a standard for Nos. 1 to 4 and No. 2 as a standard for Nos. 5 to 8. These results show that it is possible under appropriate conditions to use a standard liquid which is not necessarily the same as the sample, as contrasted with the measurements on benzene, toluene, and xylene. Attempts to use liquids and mixtures of somewhat similar specific gravity to the samples but otherwise dissimilar, such as mineral oil and water, led to errors up to 2 or more units in the third decimal place. Nitrobenzene yielded better values. Similar discrepancies were noted when benzene was used as a standard for toluene and xylene. Such properties as the temperature coefficient of expansion, the viscosity, and the surface tension might be important. The last two might affect drainage. If the first were different in the sample and in the standard, the assumption would not be justified that the specific gravity of the sample could be determined at any temperatures and the answer expressed at any other temperatures merely by using the proper value of the specific gravity of the standard at the desired temperatures.

It was found possible to use the gravitometer with a viscous liquid such as glycerol with apparently similar precision to that attainable with, for example, water. However, no statement can be made regarding the applicability of the apparatus to viscous liquids in general; each liquid under consideration should be tested separately to see if its specific gravity can be determined with the requisite accuracy.

In a series of distillation cuts such as might be obtained, for example, in fractionating a mixture of methanol, ethanol, and considerable water, no one of these substances will serve satisfactorily as a standard for all the cuts. However, a single standard may be used—for example, methanol—in testing all the cuts, if a correction curve is constructed relating the correction to the specific gravity found.

ACCURACY AND PRECISION

The standard deviation from the pycnometer value of a single value obtained by the gravitometer is $\pm 1.4 \times 10^{-4}$ specific gravity unit. This figure represents the range about the pycnometer value within which about 68% of the determined gravitometer values will lie, and, of course, by taking the average of several determinations, which can be done rapidly, an even better value may be obtained. The deviation $\pm 1.4 \times 10^{-4}$ was calculated as described in the following paragraph.

Figure 2 is a frequency distribution diagram for the magnitude of the deviation between a single value by the gravitometer and the best available value by the pycnometer. By fitting a normal distribution to the variates as given in Figure 2 (*4*) a standard deviation of $\pm 1.46 \times 10^{-4}$ was calculated. It was shown by the X^2 test that the data of Figure 2 fit satisfactorily a normal distribution with a standard deviation of $\pm 1.46 \times 10^{-4}$. Since the standard deviation includes the errors of both the pycnometer and the gravitometer, and since a standard deviation for a single value by the pycnometer could be calculated as $\pm 0.44 \times 10^{-4}$ (from the data of Table III), a standard deviation of $\pm 1.4 \times 10^{-4}$ was calculated from these data (by the square root of the differences of their squares) as the standard deviation from the pycnometer value of a single gravitometer value. By applying Student's t test it was found that there was no reason to suspect a bias or constant error between the pycnometer values and the gravitometer values.

As a measure of precision, a standard deviation of a single value by the gravitometer from the average value was calculated (from

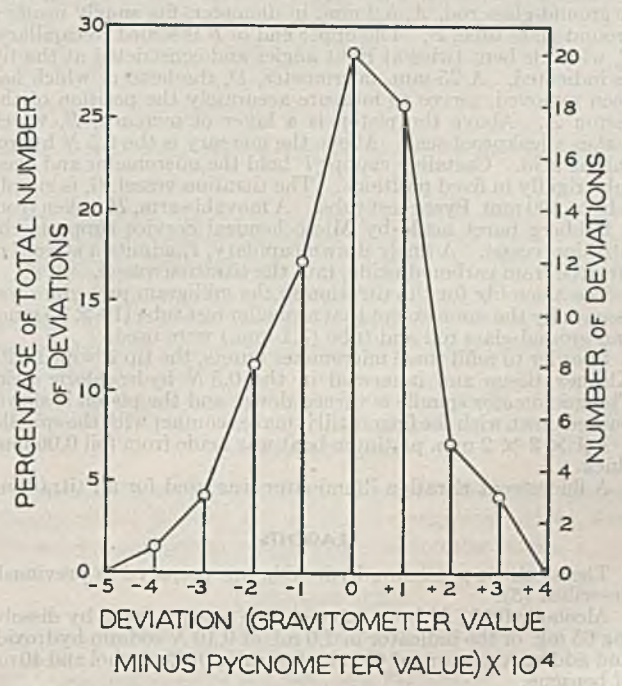

Figure 2. Frequency Distribution Diagram of Deviations of Pycnometer Values from Gravitometer Values

the data of Tables II and III) as $\pm 0.9 \times 10^{-4}$. The fact that this deviation is smaller than the above-mentioned deviation of $\pm 1.4 \times 10^{-4}$ from the pycnometer value, indicates that successive replicates agree better than replicates carried out over a longer period. Errors may be caused if both sides of the apparatus are exposed to different temperatures as by the action of drafts of air, and the poorer precision may perhaps be explained by the introduction of such variables over a period of time.

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Microdetermination of the Saponification Number of Fats and Oils

Decigram, Centigram, and Milligram Procedures

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THE literature contains no satisfactory method for the microdetermination of the saponification number of fats and oils. A semimicromethod was devised by Chargaff (*2*) but was applied to only three oils. It has been pointed out that the double-indicator method (*3*) is more easily adaptable to microprocedures than the standard method (*1*).

Methods are described for determination of the saponification number of fats and oils with samples of about 500, 50, and 5 mg.

APPARATUS

For the decigram procedure, a 10-ml. calibrated buret with 0.05-ml. graduations was used. The tip was constricted so that drops of about 0.01 ml. were delivered.

The buret for the centigram procedure is illustrated in Figure 1. A ground-glass rod, *A*, 5.2 mm. in diameter, fits snugly inside a ground-glass tube, *B*. The upper end of *B* is sealed to capillary, *C*, which is bent twice at right angles and constricted at the tip as indicated. A 25-mm. micrometer, *D*, the head of which has been removed, serves to measure accurately the position of the piston *A*. Above the piston is a layer of mercury, *E*, which makes a leakproof seal. Above the mercury is the 0.5 *N* hydrochloric acid. Castalloy clamps *F* hold the micrometer and glass tube rigidly in fixed positions. The titration vessel, *G*, is simply a 13 × 100 mm. Pyrex test tube. A movable arm, *H*, taken from a Rehberg buret made by Microchemical Service supports the titration vessel. A finely drawn capillary, *I*, admits a stream of air, free from carbon dioxide, into the titration vessel.

The assembly for the titration in the milligram procedure was essentially the same except that a smaller test tube (10 × 75 mm.) and ground-glass rod and tube (3.1 mm.) were used.

In order to refill these micrometer burets, the tip is wiped with Kleenex tissue and immersed in the 0.5 *N* hydrochloric acid. The micrometer spindle is turned down, and the piston is slowly pushed down with the fingers till it makes contact with the spindle.

A 4 × 3 × 2 mm. platinum boat was made from foil 0.06 mm. thick.

A fluorescent titration illuminator was used for all titrations.

REAGENTS

The alcoholic potassium hydroxide was prepared as previously described (*3*).

Alcoholic 0.001 *M* bromophenol blue was prepared by dissolving 65 mg. of the indicator in 1.0 ml. of 0.10 *N* sodium hydroxide and adding a mixture of 60 ml. of purified 95% alcohol and 40 ml. of benzene.

The alcohol-benzene mixture consisted of 60 ml. of reagent-grade benzene and 40 ml. of purified 95% alcohol.

Hydrochloric acid, approximately 0.5 *N*, was standardized with pure sodium tetraborate decahydrate and used in all titrations. The acid used for the centigram procedure was standardized by weighing accurately 400 to 600 mg. of a carefully prepared, approximately 0.5 weight-normal solution of borax into a 13 × 100 mm. Pyrex test tube, adding one drop of 0.001 *M* methyl red, and titrating to the first pink color. The results were expressed as milliequivalents of acid per millimeter.

The acid used for the milligram procedure was standardized analogously. About 10 mg. of pure borax were weighed on a microchemical balance and transferred to a 10 × 75 mm. Pyrex test tube. Four drops of water and one drop of 0.00008 *M* methyl red were added before the titration.

PROCEDURES

DECIGRAM PROCEDURE. Weigh accurately about 500 mg. of sample into a 50-ml. Pyrex Erlenmeyer flask. Add about 5 ml. of the alcoholic potassium hydroxide, and immediately connect a reflux condenser, the upper end of which is protected by an Ascarite tube. Boil gently for 30 minutes. Add 2 drops of 1% alcoholic phenolphthalein, and titrate with 0.5 *N* hydrochloric acid to the disappearance of the pink color. Add 3 drops (0.18 ml.) of aqueous 0.001 *M* bromophenol blue and 1 ml. of benzene. Continue the titration to a green color that does not turn blue on further agitation.

CENTIGRAM PROCEDURE. Weigh with an accuracy of 0.02 mg. about 50 mg. of sample into a tared Pyrex test tube, add about 21 drops (0.5 ml.) of alcoholic potassium hydroxide, and immediately attach an Ascarite tube. Support the tube vertically, so that the bottom rests on the flat surface of a micro drying block which is kept at 145° ± 5°. The test tube serves as both reaction vessel and reflux condenser. The saponification is complete in 30 minutes. Add 1 drop (0.03 ml.) of 0.2% alcoholic phenolphthalein. Insert the tip of the micrometer buret (previously wiped with Kleenex tissue) and the tip of the air-delivery tube, and support the tube in the titration apparatus (Figure 1). Adjust the air stream to a rate of about 80 bubbles per minute. Add the 0.5 *N* hydrochloric acid by carefully turning the micrometer spindle until the color just disappears. Read the micrometer at this point.

Without removing either capillary from the test tube, add 1 drop (0.06 ml.) of aqueous 0.001 *M* bromophenol blue and 7 drops (0.12 ml.) of benzene. Decrease the air stream to about 50 bubbles per minute, and continue the titration till the solution has a milky appearance; then add 7 more drops of benzene, and increase the air stream to about 100 bubbles per minute. Continue the titration to a green end point. The hydrochloric acid

used between the two end points is equivalent to the potassium hydroxide that was required for the saponification.

MILLIGRAM PROCEDURE. Weigh the platinum boat (4 × 3 × 2 mm.) on a microchemical balance, then place it on a clean surface. Dip the tip of a finely drawn glass rod into the sample, let most of the oil drain off the rod, and touch the center of the boat with the tip of the rod. Transfer the boat to the balance pan, and weigh it again. The sample should be between 3 and 8 mg. With platinum-tipped forceps, place the boat just inside the open end of a horizontally held 10 × 75 mm. Pyrex test tube. Then tilt the test tube so that the boat slides to the bottom of the tube. If any oil sticks to the side of the tube, the determination must be started anew.

Let 2 drops of the alcoholic potassium hydroxide fall directly from the siphon of the storage bottle into the bottom of this test tube. Immediately connect an Ascarite tube to the test tube. Then support it with a clamp and ring stand so that the bottom of the tube rests on the flat surface of a micro drying block heated to 130° ± 5°.

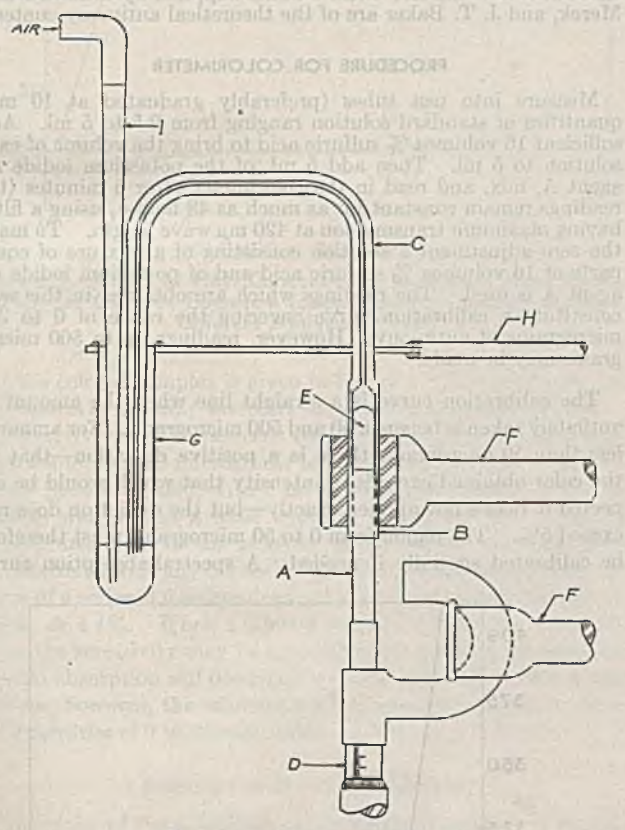

Figure 1. Micrometer Buret

After 30 minutes, remove the Ascarite tube and add 2 drops (0.06 ml.) of 0.02% alcoholic phenolphthalein. Immediately insert the tip (previously wiped with Kleenex tissue) of the micrometer buret and the tip of the air-delivery tube, and support the tube in the titration apparatus (Figure 1). Take care that the boat does not interfere with the delivery of acid from the buret. Adjust the air stream to about 60 bubbles per minute. Note the reading, a, of the micrometer before any hydrochloric acid is added to the titration vessel. Now titrate to the disappearance of the pink color of the phenolphthalein. Rinse the inside of the test tube with 0.10 to 0.20 ml. of the alcohol-benzene mixture by means of a measuring pipet. If the pink color reappears, add more hydrochloric acid till it disappears again. Note this reading, b, of the micrometer. Add 2 drops (0.06 ml.) of the alcoholic bromophenol blue. Continue the titration. Just before the end point is reached, rinse the inside of the test tube again with 0.10 to 0.20 ml. of the alcohol-benzene mixture. Note the micrometer reading, c, when the green end point is reached.

Contamination of the alcoholic potassium hydroxide by carbon dioxide of the air could not be avoided in the milligram procedure, although no difficulty was encountered in this respect in the other procedures. Therefore a blank correction must be applied in the milligram procedure. To run the blank, put 2 drops of the alcoholic potassium hydroxide into the Pyrex test tube and titrate it as described above, noting the initial micrometer reading, x, the reading at the phenolphthalein end point, y, and the reading at the end point of bromophenol blue, z. Then calculate the saponification number with the equation

$$S = \frac{[(b - c) - B(a - c)]56.11\,F}{W}$$

where S = saponification number

$$B = \frac{y - z}{x - y}$$

F = concentration of hydrochloric acid, milliequivalents per mm.

W = weight of sample, grams

RESULTS

The saponification numbers of eleven oils were determined by the standard method (*1*) and by each of the methods described in this paper. Each entry in Table I denotes a single determination except as indicated in the footnotes. No values were omitted except those obtained before the methods had been perfected.

DISCUSSION

Excellent results are obtained by the decigram and centigram methods, while the milligram method yields very satisfactory results. In order to study the precision of the methods, one oil was run several times by the same method. The mean deviations were 0.3, 0.1, and 0.5 unit by the decigram, centigram, and milligram methods, respectively.

Table I. Comparison of Results by Various Methods

Oil	Saponification No. Standard method	Saponification No. Decigram method	Difference	Saponification No. Centigram method	Difference	Saponification No. Milligram method	Difference
Castor oil	181.5	181.5	0.0	182.0	+0.5	182.4	+0.9
Cocoa butter	194.6	194.5	−0.1	195.0	+0.4	195.4	+0.8
Coconut oil	258.6	258.9	+0.3	258.5	−0.1	259.2	+0.6
Cod liver oil	188.0	188.6	+0.6	187.9	−0.1	188.2[a]	+0.2
Corn oil	191.6	191.6[b]	0.0	191.6[a]	0.0	192.1	+0.5
Lard oil	195.5	195.6	+0.1	195.7	+0.2	196.2	+0.7
Linseed oil	187.0	187.1	+0.1	187.4	+0.4	187.4	+0.4
Neat's-foot oil	186.7	186.7	0.0	186.4	−0.3	187.4	+0.7
Olive oil	191.5	191.8	+0.3	192.0	+0.5	190.7	−0.8
Rapeseed oil	174.3	174.0	−0.3	174.6	+0.3	175.2	+0.9
Tung oil	194.7	194.5	−0.2	194.4	−0.3	195.0	+0.3
Mean (signs disregarded)			±0.2		±0.3		±0.6

[a] Mean of 4 determinations.
[b] Mean of 10 determinations.

The decigram method is more convenient than the gram method chiefly because the smaller solution cools almost instantaneously after saponification and reduces the waiting period. The centigram procedure is probably a little more troublesome because of the special buret. The milligram procedure is still more troublesome and is to be chosen only when the quantity of sample is very limited.

None of these methods is applicable to acetylated oils (*3*).

ACKNOWLEDGMENT

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Colorimetric Micromethod for Determination of Antimony in Biological Materials

With Concomitant Determination of Bismuth

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A colorimetric method for the determination of antimony in biological materials is presented. The material is digested in sulfuric acid with the addition of nitric acid or of a mixture of nitric and perchloric acids. The diluted digest is treated with a solution containing potassium iodide and ascorbic acid; the color of the potassium iodoantimonite complex is determined in a photoelectric colorimeter. The standard error is about 2%, and the recoveries of added antimony are usually within ±2%. Quantities as small as 10 micrograms may be estimated, but the error here is somewhat larger. Bismuth gives the same color reaction as antimony. However, if it is present, it may be quantitatively determined on the same digest, and by subtraction the amount of antimony may be estimated.

PROGRESS in the experimental study of the organic compounds of antimony has thus far been limited by the lack of a simple and accurate method for the determination of the amounts of that element likely to be found in the body tissues, fluids, and excreta, particularly the urine (*3*). The method of Christiansen (*1*) is applicable to all types of biological material but requires the presence of rather large amounts of antimony. Hassan (*6*) has published a technically involved method which he applied to urine only. The rhodamine B method of Fredrick (*4*) is very specific, and accurate, but is also technically complicated; while it could undoubtedly be adapted to biological material, the author did not so apply it. Very recently Webster and Fairhall (*8*) have employed the same reagent for the determination of microquantities of stibine.

An excellent lead for a method has been provided by the work of Fauchon (*2*). He has shown that the addition to solutions of Sb^{III} of a reagent consisting of a solution 10% in both sulfuric acid and potassium iodide yields the yellow complex, $KSbI_4$, which can be determined colorimetrically. From these observations the present method has been developed.

In this work it has been deemed more practicable to add the sulfuric acid and the potassium iodide separately rather than as a single reagent, for two reasons: (1) the reagent described by Fauchon is very unstable, and (2) in the acid digests of biological material which it was proposed to use in this work, sulfuric acid would already be present. Its concentration in these digests could readily be adjusted to the proper point as determined experimentally, and it could therefore be omitted from the color reagent.

REAGENTS

Sulfuric acid, specific gravity 1.17, $\frac{20°}{4°}$ C., 160 ml. of concentrated acid diluted to 1 liter with distilled water (referred to below as 16 volumes % sulfuric acid).

Potassium iodide reagent A, 112 grams of C.P. potassium iodide and 20 grams of crystalline ascorbic acid dissolved in distilled water to make 1 liter. This reagent is made up only as needed and is kept in a brown bottle, but is stable for about one month. It must be discarded when molds develop.

Potassium iodide reagent B (for bismuth determination), 16 grams of C.P. potassium iodide and 20 grams of ascorbic acid dissolved in distilled water to make 1 liter. This reagent must be prepared freshly about once each week.

Perchloric acid–nitric acid mixture, 3 volumes of 70% perchloric acid mixed with 1 volume of concentrated nitric acid.

Hydrogen peroxide, 30% solution.

STANDARD SOLUTION

Dissolve 110 mg. of C.P. potassium antimony tartrate in 500 ml. of distilled water, add 160 ml. of concentrated sulfuric acid, cool, and dilute to 1 liter with distilled water. One milliliter of this solution contains 40 micrograms of antimony. Fredrick has shown that the C.P. tartar emetics supplied by Mallinckrodt, Merck, and J. T. Baker are of the theoretical antimony content

PROCEDURE FOR COLORIMETER

Measure into test tubes (preferably graduated at 10 ml.) quantities of standard solution ranging from 0.5 to 5 ml. Add sufficient 16 volumes % sulfuric acid to bring the volume of each solution to 5 ml. Then add 5 ml. of the potassium iodide reagent A, mix, and read in the colorimeter after 5 minutes (the readings remain constant for as much as 48 hours), using a filter having maximum transmission at 420 mμ wave length. To make the zero adjustment a solution consisting of a mixture of equal parts of 16 volumes % sulfuric acid and of potassium iodide reagent A is used. The readings which are obtained in this way constitute a calibration curve covering the range of 0 to 200 micrograms of antimony. However, readings up to 500 micrograms may be made.

The calibration curve is a straight line when the amount of antimony taken is between 50 and 500 micrograms. For amounts less than 50 micrograms there is a positive deviation—that is, the color obtained exceeds in intensity that which would be expected if Beer's law applied exactly—but the deviation does not exceed 5%. The region from 0 to 50 micrograms must therefore be calibrated specially if needed. A spectral-absorption curve

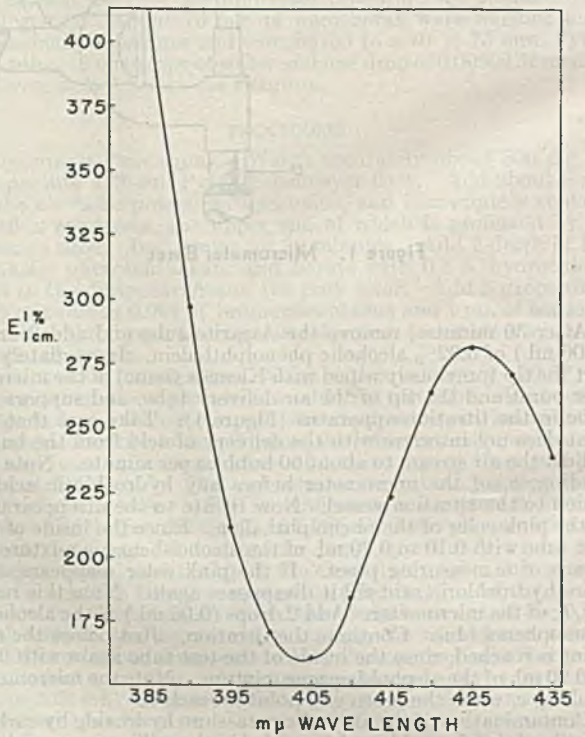

Figure 1. Partial Spectral-Absorption Curve of Potassium Iodoantimonite

Concentration expressed in terms of antimony

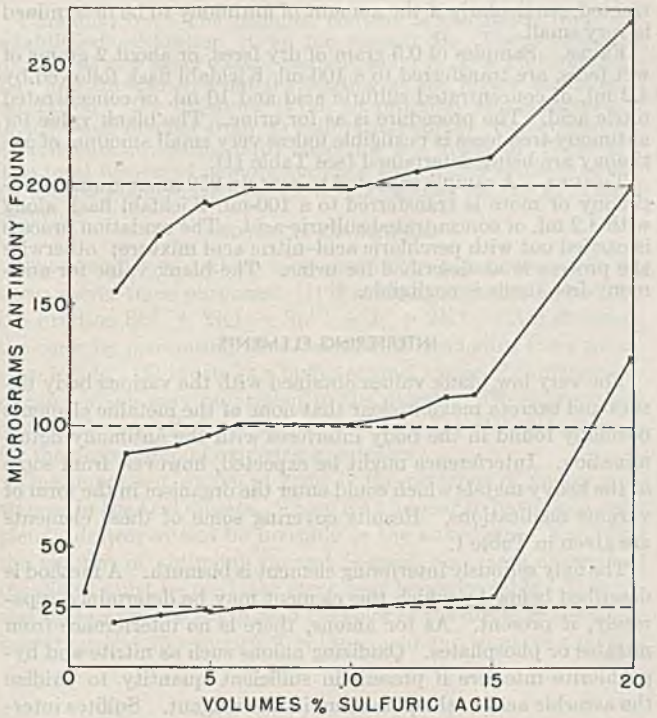

Figure 2. Effect of Final Concentration of Sulfuric Acid on Intensity of Color of Potassium Iodoantimonite Complex at Three Different Antimony Levels

for the colored complex is given in Figure 1. The maximum absorption is at 425 mμ; therefore the usual 42 filter may be used.

SENSITIVITY. The per cent transmission at 420 mμ of a solution containing 10 micrograms of antimony (in 5 ml. of 16 volumes % sulfuric acid, with 5 ml. of potassium iodide reagent A added) was 90.4 at a band width of 0.6 to 0.7 mμ. Thus 10 micrograms is about the smallest amount which one could hope to determine with any degree of accuracy; the observed standard error of a series of 6 estimations of 10 micrograms was 0.44 microgram, or 4.4%. When a Klett-Summerson instrument is available, the sensitivity may be approximately doubled by using the special absorption cell described by Giacomino (*5*). This would require, however, the establishment of another calibration curve for quantities of 0 to 50 micrograms.

EFFECT OF ACID CONCENTRATION

The color of the potassium iodoantimonite complex is materially influenced by the concentration of sulfuric acid, as is shown in Figure 2. The optimal concentration for quantitative work would appear to be 8 volumes %—that is, 16 volumes % in the acid digest of biological material—since over the range 6.3 to 9.7 volumes % there is no change in the intensity of color of the antimony complex. In fact, such extreme concentrations as 5 and 13 volumes % alter the color only to 95 and 105%, respectively, of that obtained at 8 volumes % concentration. A similar situation in the case of potassium iodobismuthite has been noted by Sproull and Gettler (*7*).

The acid concentration is kept within the desired range by the simple expedient of starting the digestion process within an amount of sulfuric acid which exceeds slightly that required to give 16 volumes % solution when finally diluted—for example, 4.2 ml. of concentrated sulfuric acid when diluted to 25 ml. gives a 16.7 volumes % solution. This amount of acid is therefore taken where a final dilution to 25 ml. is planned, and makes allowance for a loss of 0.2 ml. of acid during the digestion process. If a dilution to 10 ml. is planned, only 1.8 ml. of sulfuric acid are used for the digestion. This, again, makes allowance for a loss of 0.2 ml. Actual titrations of a number of digests have shown them to fall within the range 14.8 to 16.7 volumes %. It is obvious that excessive boiling of the digest, after the water has been driven off, must be avoided. For very accurate work the digests should be checked for sulfuric acid concentration unless the antimony concentration permits their dilution with known 16 volumes % acid.

EFFECT OF IODIDE CONCENTRATION

To achieve a concentration of potassium iodide equivalent to that used by Fauchon would require a reagent containing 16% of the salt—that is, 8% in the solution used for colorimetry. This concentration does, in fact, appear to give the maximum sensitivity (Figure 3, *A*). However, when the concentration is reduced stepwise the interesting fact is revealed that the antimony color begins to diminish rapidly, and at low concentrations disappears entirely. At the same time the bismuth color, which is also maximal when the reagent contains 16% of potassium iodide, loses only about 10% of its intensity (Figure 3, *B*). When the reagent contains 1.6% of potassium iodide, antimony gives no color whatsoever, and bismuth may be determined by what is essentially the Sproull and Gettler method. At 11.2% of potassium iodide the bismuth and antimony colors are exactly additive (Figure 3, *C*) and this has furnished a basis for the determination of both elements on the same digest.

METHODS OF ANALYSIS FOR ANTIMONY

BLOOD PLASMA. Ten milliliters or less are measured accurately into a 100-ml. Kjeldahl flask, followed by 1.8 ml. of concentrated sulfuric acid and 5 ml. of a 3 to 1 perchloric-nitric acid mixture. Digestion is now carried out over a low flame, with addition of more of the oxidizing solution from time to time in order to prevent carbonization. When the oxidation is complete the digest is cooled, and 30 ml. of water are added and boiled off (to the appearance of fumes of sulfur trioxide). The digest is now accurately diluted to 10 ml. (For this operation, add 3 ml. of water to the digest and cool under the tap. Transfer quantitatively to a test tube graduated at 10 ml., using a 3-ml. pipet for the transfer. Rinse the sides of the flask with 2 ml. of water and transfer to the test tube. Repeat, then dilute with water to the mark.) To an aliquot an equal volume of potassium iodide reagent A is added. (A precipitate of potassium perchlorate may appear at this point. If so, it is centrifuged out.)

If the color obtained is beyond the readable range, the digest is diluted accurately with 16 volumes % sulfuric acid until a readable value is obtained. For a blank, the mixture of equal volumes of 16 volumes % sulfuric acid and potassium iodide reagent A is used. However, the digestion of a similar amount of antimony-free serum will give a small reading, which must be subtracted if accurate results are to be obtained on very low antimony concentrations.

URINE. Measure accurately into a 100-ml. Kjeldahl flask 25 ml. of urine and 4.2 ml. of concentrated sulfuric acid. Add approximately 10 cc. of concentrated nitric acid and boil gently over a small flame. Add more nitric acid from time to time to avoid carbonization. (The purpose of this is to avoid reduction of Sb^{V} to Sb^{III} in the presence of chloride, since antimony trichloride is slightly volatile.) When the oxidation is complete the digest is cooled and about 50 ml. of water are added and boiled off. At this stage the digest should not have any yellow color; if it does,

Table I. Interference of Some Metallic Elements with Determination of Antimony[a] as $KSbI_4$

Element Added	Amount Added	Antimony Found
	Micrograms	*Micrograms*
As^{III}	100	100
Hg^{II}	100	100
Bi^{III}	100	242
Fe^{II}	200	101
Cu^{II}	100	100
Pb^{II}[b]	200	102
W^{VI}[b]	200	99
Tl^{I}[b]	200	82[c]

[a] 100 micrograms.
[b] These elements were included at the suggestion of W. G. Fredrick. Tungsten and thallium interfere with the rhodamine B procedure for antimony.
[c] Forms a yellow precipitate which can be removed by centrifugation. Apparently some potassium iodoantimonite is adsorbed on precipitate.

Table II. Recovery of Antimony Added to Biological Materials

Material	Antimony Added[a]	Antimony Recovered[b], (Mean)	Standard Error of Mean[c]
	Micrograms	*Micrograms*	%
Beef blood plasma, 10 ml.	0	3	....
	12.5	12.7	13.5
	100	99	2.9
	500	516	1.7
	1250	1275	2.1
Human urine, 25 ml.	0	10	....
	250	255	2.2
	750	728	1.7
	1250	1253	2.7
	5000	5040	0.7
	1765[d]	1770	1.4
	2360[e]	2300	1.8
Dry rabbit feces, 0.5 gram	0	3	....
	250	249	3.5
	2500	2544	1.3
Rabbit liver (fresh), 2.5 grams	0	0	....
	250	244	2.0
	2500	2450	1.2

[a] As tartar emetic except where otherwise indicated.
[b] After subtraction of established blank.
[c] From mean.
[d] As Neostibosan, a preparation containing *p*-aminophenylstibonic acid, its acetyl derivative, and antimonic acid.
[e] As Stibanose, a preparation containing the complex of sodium gluconate and antimonic acid as the diethyl monoethanolamine salt. The antimony analysis of this compound and of Neostibosan was kindly supplied by H. B. Corbitt of the Winthrop Laboratories.

a few drops of Superoxol or of nitric-perchloric acid mixture are added to the hot solution and the boiling is continued for another minute. The digest is now diluted to 25 ml. and a 5-ml. portion (which contains about 16 volumes % sulfuric acid) is taken for colorimetric analysis as for blood plasma. If the amount of antimony exceeds that which can be read, the digest is diluted with 16 volumes % sulfuric acid until a readable color is obtained. (Or the colored solution may simply be diluted with the sulfuric acid–potassium iodide solution—which is used for the blank—until the color is within the readable range.) A blank determination on 25 ml. of antimony-free urine must be run and subtracted, particularly if the amount of antimony to be determined is very small.

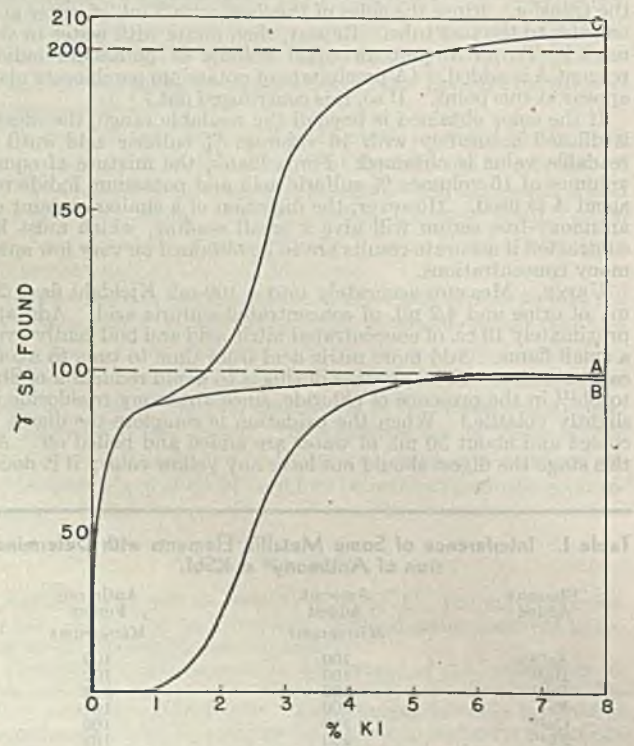

Figure 3. Effect of Final Concentration of Potassium Iodide on Intensity of Color

A. 100 micrograms of antimony
B. 70 micrograms of bismuth
C. 100 micrograms of antimony and 70 micrograms of bismuth

In all cases 100 is taken as the amount of color obtained when 100 micrograms of antimony in 5 ml. of 16 volume % sulfuric acid are mixed with 5 ml. of a solution containing 16% potassium iodide and 2% ascorbic acid

FECES. Samples of 0.5 gram of dry feces, or about 2 grams of wet feces, are transferred to a 100-ml. Kjeldahl flask followed by 4.2 ml. of concentrated sulfuric acid and 10 ml. of concentrated nitric acid. The procedure is as for urine. The blank value for antimony-free feces is negligible unless very small amounts of antimony are being determined (see Table II).

TISSUES. A sample expected to contain 250 micrograms of antimony or more is transferred to a 100-ml. Kjeldahl flask along with 4.2 ml. of concentrated sulfuric acid. The oxidation process is carried out with perchloric acid–nitric acid mixture; otherwise the process is as described for urine. The blank value for antimony-free tissue is negligible.

INTERFERING ELEMENTS

The very low blank values obtained with the various body tissues and excreta make it clear that none of the metallic elements normally found in the body interferes with the antimony determination. Interference might be expected, however, from some of the heavy metals which could enter the organism in the form of various medications. Results covering some of these elements are given in Table I.

The only seriously interfering element is bismuth. A method is described below by which this element may be determined separately, if present. As for anions, there is no interference from nitrates or phosphates. Oxidizing anions such as nitrite and hypochlorite interfere if present in sufficient quantity to oxidize the ascorbic acid in the potassium iodide reagent. Sulfites interfere in any concentration, since they give a yellow color when added to a reagent blank.

RECOVERY OF ANTIMONY FROM BIOLOGICAL MATERIALS

The results of recovery experiments are given in Table II. The values obtained are satisfactorily precise, as is shown by the standard errors. As a matter of fact, these errors are ordinarily no greater than would be obtained in setting up and reading a series of half a dozen standards of the same antimony concentration. The recovery experiments have included several forms of the element. In most cases the antimony was added as tartar emetic, but in some cases organic compounds such as Neostibosan and Stibanose were added.

METHOD FOR DETERMINING BOTH ANTIMONY AND BISMUTH

The colorimeter must be accurately calibrated for bismuth using both the 1.6 and 11.2% potassium iodide reagents. A given amount of bismuth yields 11% more color at the higher iodide concentration.

An aliquot of the digest is treated with an equal volume of reagent B and another aliquot is treated with an equal volume of reagent A. Both are read in the colorimeter against a blank consisting of one volume of 16 volumes % sulfuric acid and one volume of potassium iodide reagent A. The first aliquot gives the amount of bismuth present, and the second gives antimony plus bismuth. If the second reading is beyond the range of the instrument, the digest is diluted with 16 volumes % sulfuric acid until a readable color can be obtained with reagent A, then both determinations are repeated.

Table III. Recovery of Antimony and Bismuth from Biological Materials

Material	Bismuth Added[a]	Antimony Added[b]	Bismuth Recovered ± Standard Error	Antimony Recovered ± Standard Error
	Micrograms		*Micrograms*	
Human urine, 25 ml.	600	600	594 ± 29.0	617 ± 26.0
	1000	200	981 ± 8.6	214 ± 17.0
	200	1000	214 ± 10.5	986 ± 14.0
	200	200	205 ± 6.5	201 ± 6.0
Beef blood plasma, 10 ml.	50	50	48.7 ± 1.8	49.2 ± 3.3
	100	100	96.5 ± 3.0	104.0 ± 5.3
	200	200	203 ± 3.5	204.5 ± 3.9

[a] As bismuth nitrate.
[b] As potassium antimony tartrate.

CALCULATION. The bismuth content is calculated from the established calibration curve for reagent B. The colorimeter reading at the lower iodide concentration is then multiplied by 1.11 and subtracted from the reading at the higher iodide concentration. The difference is due to antimony and is calculated in the usual manner from its calibration curve. Some recovery experiments involving both elements are given in Table III. The total recovered is more accurate than either element alone; an accuracy better than ±5% is not claimed for the individual elements.

DISCUSSION OF METHOD

The ascorbic acid which is present in the potassium iodide reagent serves three purposes: (1) it reduces the iodine formed by the reaction $Sb^{V} + 2KI \rightarrow Sb^{III} + I_2 + 2K^{+}$; (2) it stabilizes the color by preventing the formation of free iodine from potassium iodide; (3) it acts as a buffer against traces of oxidizing impurities which may be present in the digests. These properties of ascorbic acid eliminate the necessity for any elaborate process for the destruction of oxidizing impurities.

One important source of error is the presence of yellow substances in the acid digests. These may appear to have been completely destroyed and be invisible to the naked eye. Yet when the amount of antimony present is small and large aliquots of the digest must be used, the error may be appreciable. It is advisable as a precaution to read the color of the digest in the colorimeter against 16 volumes % sulfuric acid and to make a correction appropriate to the aliquot used. If the aliquot used is as little as 1 ml. this factor is usually negligible.

The only other technical points which require attention—namely, control of acid concentration, and avoidance of loss of antimony as antimony trichloride—have been sufficiently emphasized.

ACKNOWLEDGMENT

The author is indebted to W. G. Fredrick for a number of constructive suggestions which have added materially to the value of this paper, and to G. E. Ewing of the Winthrop Laboratories for making the measurements on the Beckman spectrophotometer.

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Microdetermination of Mercury in Biological Material

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A procedure suitable for determining minute quantities of mercury in biological and related materials is described. Organic matter is destroyed by digesting the sample in a special apparatus, by boiling first with a mixture of sulfuric and nitric acids, followed by a second boiling treatment after addition of potassium permanganate. Mercury is extracted from the decolorized acid-permanganate digest (diluted to 1.8 *N* in respect to sulfuric acid) by means of a chloroform solution of di-β-naphthylthiocarbazone. The chloroform extract is then treated with a sulfuric acid–sodium thiosulfate mixture to separate the mercury from copper. The final estimation of mercury is made by photometering di-β-naphthylthiocarbazone–chloroform extracts of the copper-free aqueous phase following treatment with potassium permanganate. At least 50 grams of blood must be used for the reliable estimation of concentrations as low as 1 microgram of mercury in 100 grams of blood. A table, which compares the mercury content of the blood and urine of exposed persons, shows that the mercury content of the blood is very low. Except in one case, the amounts were well below 10 micrograms for 100 grams of blood. The highest, 0.029 mg. per 100 grams, was found in a case where the urine level was 4.44 mg. of mercury per liter. The mercury–di-β-naphthylthiocarbazone complex is more stable than the analogous dithizone complex.

SATISFACTORY methods for the determination of minute quantities of mercury, particularly in the air of industrial establishments and in the urine of exposed persons, have been described (*3, 4, 8, 11, 12*). The most sensitive of these methods involving the scattering of the radiation at 2537 Å. by mercury vapors (*3, 12*) is very satisfactory for air analysis, but its application in the analysis of other material requires special equipment and inconvenient preparatory procedures. Ballard and Thornton (*1*) have applied the method to the determination of minute quantities of mercury in aqueous solutions and have mentioned the possibility of its use in the analysis of biological material, but have given no data or details of procedure on such applications. Laug and Nelson (*6*) have described a simple chemical method based upon the use of dithizone for the general analysis of biological material, but the authors were unable to apply the method successfully whenever it was necessary to employ all of a large sample. Others (*10*) also have reported difficulties in the use of the Laug and Nelson method.

The colorimetric method founded upon the use of di-β-naphthylthiocarbazone (*4*) has been employed successfully by the authors in the analysis of samples of air, urine, and aqueous solutions of organic materials which can be oxidized conveniently by digestion with acid-potassium permanganate. In applying the method to the analysis of other material, however (solid tissues, blood, etc.), difficulties were encountered mainly because of losses of mercury due to the methods used in oxidizing the organic matrix. The general applicability of the method depended therefore upon the development of safe oxidation procedures and upon the introduction of modifications in the extraction steps which would eliminate the need for using small samples or aliquots in order to protect the mercury extraction agent. Such a convenient procedure has been developed and is given below in such detail as to involve some slight repetition of earlier published work (*4*) for the sake of completeness.

REAGENTS

Oxidizing Mixture. A 1 to 1 mixture of concentrated sulfuric and nitric acids is convenient to use for the destruction of organic matter.

Hydroxylamine Hydrochloride, 50 and 5% w/v solutions.

Potassium Permanganate, 5-grain (0.325-gram) tablets and a saturated solution.

Sodium Thiosulfate, 1.5 grams of sodium thiosulfate in 100 ml. of water.

Di-β-naphthylthiocarbazone. (1) Initial extraction solution, 20 mg. of di-β-naphthylthiocarbazone in 1 liter of chloroform. (2) Final extraction solutions, 0 to 5 micrograms range 6 mg. of di-β-naphthylthiocarbazone per 1 liter of chloroform; 0 to 50 micrograms range same as initial extraction solution.

The extraction solutions are stabilized and used chloroform is reclaimed by procedures described by Bambach and Burkey (*2*)

PROCEDURE

Preparation of Samples. Urine (and aqueous solutions of most organic materials). Fifty-milliliter samples are digested with sulfuric acid and potassium permanganate in a boiling flask provided with a "cold finger" as previously described (*4*).

Air Samples. Atmospheres may be sampled either by passing the air at a suitable rate through a gas scrubber containing 100 ml. of a solution of potassium permanganate (10 grams) in 10% (v/v) sulfuric acid, or the sample may be collected in an evacuated balloon flask (*7*) and the mercury brought into solution by introducing 100 ml. of the absorbent medium into the flask and shaking it for a few minutes. The entire sample or a suitable aliquot may be used, but only after decolorizing the solution with hydroxylamine hydrochloride solution (50% w/v).

Solid Tissue and Blood. Introduce the sample (1 to 50 grams) into a 1-liter, two-necked, distilling flask (Figure 1), add 40 ml. of the oxidizing mixture, insert the cold finger, and heat the mixture to boiling. After boiling for 2 hours, cool, then further chill the solution by immersing the flask in an ice bath. Remove the fats and fatty acids which separate out, by filtering the solution through a glass-wool plug inserted into the neck of a funnel. Collect the clear filtrate in a second 1-liter, two-necked flask, reinsert the finger, add two 5-grain tablets of potassium permanganate, and again heat the solution to boiling. Continue boiling and add tablets of potassium permanganate (2 at a time), through the second neck of the flask, either until a precipitate of manganese dioxide persists or until 8 to 10 tablets have been used for each 10 grams of sample. Cool the flask again in an ice bath and add 5 ml. of hydroxylamine hydrochloride solution (50% w/v) to decolorize the solution. If, on cooling, fats again separate out, filter the solution as after the first chilling.

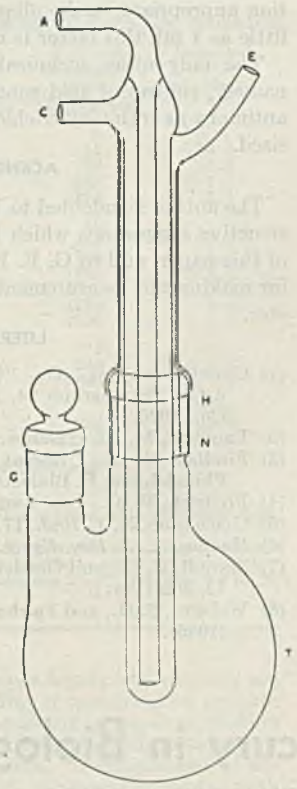

Figure 1. Digestion Apparatus Used in Oxidation of Organic Material

Height of apparatus, 40 cm.

A. Water inlet
C. Water outlet
E. Gas outlet
G. 24/40 T
H. 34/45 T
N. 1.5- to 2-mm. gas gap
T. 1-liter Pyrex flask

Initial Extraction. Proceed with the extraction of mercury from samples of digested urine as directed previously (*4*). Solutions resulting from air sampling, containing not more than 10% (v/v) sulfuric acid, may be handled in a similar fashion. In all cases in which 40 ml. of the oxidizing mixture have been used, transfer the prepared sample to a 500-ml., pear-shaped, separatory funnel, dilute it to 400 ml. with distilled water, add 5 ml. of hydroxylamine hydrochloride solution (50% w/v), and extract the mercury with 5-ml. portions of initial extraction di-β-naphthylthiocarbazone solution. Continue extraction with 5-ml. portions of di-β-naphthylthiocarbazone solution until the last portion added shows no change in color, collecting the extracts in a second 150-ml. Squibb separatory funnel. (Each 5-ml. portion of di-β-naphthylthiocarbazone solution extracts approximately 25 micrograms of mercury and the total quantity of di-β-naphthylthiocarbazone used indicates the concentration range, thereby determining the final dilution of the sample and the size of the cell which is to be used for photometric purposes. If minute traces of mercury are expected, the individual portions of extracting solution used may be reduced to 1 or 2 ml. in volume in order to make more certain by the color change that less than 5 micrograms of mercury are present.)

To the combined chloroform extracts or to an aliquot containing not in excess of 50 micrograms of mercury in the second funnel, add 50 ml. of dilute sulfuric acid (2% v/v) and 4 ml. of the sodium thiosulfate solution. Shake for 1 minute and discard the chloroform layer. Wash the aqueous solution twice with 5-ml. portions of clear chloroform and then transfer the aqueous layer to a 200-ml. boiling flask. Add 5 ml. of saturated potassium permanganate solution, insert a cold finger in the mouth of the flask (*4*), and heat the solution for 10 minutes. Cool the solution and decolorize it by adding aqueous hydroxylamine hydrochloride (5% w/v) dropwise, and then add 1 ml. in excess. Reinsert the condenser and heat just to the boiling point. Cool and rinse the solution into a 150-ml. Squibb-type separatory funnel.

Final Colorimetric Extraction. Dilute the solution to 100 ml. and extract the mercury with di-β-naphthylthiocarbazone solution, using 20 ml. of the initial extraction solution for the range 0 to 50 micrograms, or 10 ml. of the 6 mg. per liter solution for the 0 to 5 micrograms range. For photometric readings in the lower range of concentrations a cell of 50-mm. light path is employed, while for the higher a cell of 10-mm. light path is satisfactory. Any suitable photometer capable of using Style D American Instrument Company cells may be used. Filters for photometers that require them should be centered at 515 mμ.

Working curves are obtained with known quantities of mercury (as the nitrate) plus 50 ml. of sulfuric acid (2% v/v) and 1 ml. of hydroxylamine hydrochloride solution (5% w/v) diluted to 100 ml. as in the final colorimetric extraction step.

RESULTS

The recoveries in the case of known quantities of mercury added to blood and tissue samples (liver) are listed in Tables I and II. Table III gives some results obtained upon samples of the blood and urine of exposed persons in order to illustrate the relationships between the blood and the urine with respect to concentration of mercury. These data demonstrate the practical need for a micromethod capable of using such relatively large samples.

DISCUSSION

As is indicated in Table I, it is possible to detect as little as 0.5 microgram of mercury in 50 grams of blood, this being the smallest quantity of sample that can be employed successfully when the concentration of mercury is of the order of 1 microgram per 100 grams. Mercury cannot be extracted from acid digests of such large samples, prepared by the Laug and Nelson method (*6*), either because of the large quantity of nitric acid which must be used or because in the oxidation of the organic matter certain products are produced which destroy the extracting agent (di-

Table I. Recoveries of Mercury Added to Blood Samples

Blood	Tablets of $KMnO_4$ Employed	Mercury Added	Mercury Found
Grams		*Micrograms*	*Micrograms*
50	40	0	1, 0.8 (0.9 av.)
20	20	0	0.7, 0.5 (0.6 av.)
50	40	0.5	1.4, 1.4
50	40	1.0	1.6, 2.0
50	40	5	5.9, 5.3
50	40	10	11, 11
50	40	20	21, 20
20	20	50	50, 50.5
20	20	500	505, 495

Table II. Recoveries of Mercury Added to Rabbit Liver

Liver Used	Tablets of $KMnO_4$ Employed	Mercury Added	Mercury Found
Grams		*Micrograms*	*Micrograms*
50	40	0	3.8, 2.6 (3.2 av.)
50	40	5	8.4, 8.4
50	40	100	101, 102.5

Table III. Concentration of Mercury in Blood and Urine of Exposed Persons

Number	Urine	Blood	
	Mg./l.	*Grams*	*Mg./100 g*
J.S.	0.12	55.6	0.001
W.H.	1.06	50.3	0.009
L.P.	1.20	33.5	0.006
O.M.	0.82	33.4	0.003
L.W.	0.04	58.5	0.001
H.M.	4.44	47.7	0.029
M.B.	0.64	32.4	0.001
J.W.	0.18	53.7	0.001

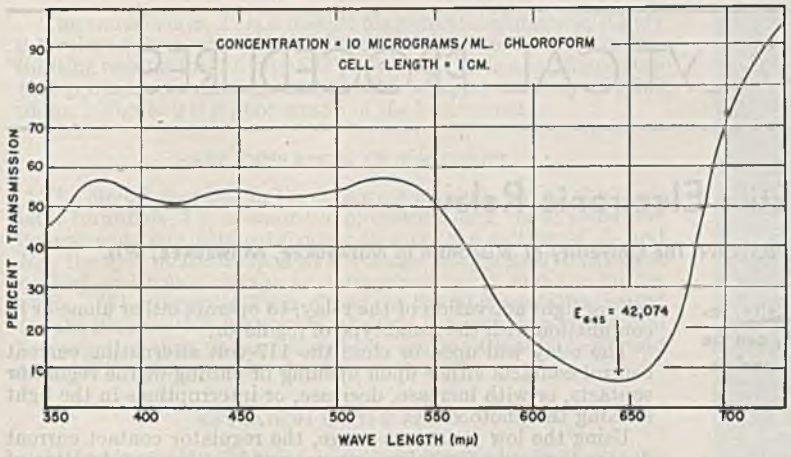

Figure 2. Transmission Curve for Twice Repurified Di-β-naphthylthiocarbazone in Chloroform

chizone or di-β-naphthylthiocarbazone). The use of potassium permanganate in the authors' method overcomes these difficulties, for not only does this additional treatment destroy more of the organic matter, but in the process of doing so it neutralizes some of the acid (probably much of the nitric acid) and permits extraction of the mercury without decomposition of the extracting agent. The use of the additional reagent increases the magnitude of the reagent blank, but not to such an extent as to be practically disadvantageous. The total blank associated with the employment of 40 ml. of the standard oxidizing mixture has been found to be 0.9 and 0.6 microgram, respectively, when 40 and 20 tablets of potassium permanganate are used.

The dilution of the prepared sample to the volume of 400 ml. also tends to prevent oxidation of the di-β-naphthylthiocarbazone and reduces the concentration of acid therein (in terms of sulfuric acid employed) to about 1.8 *N*, which is of the order of that (1.5 *N*) used by Laug and Nelson (*6*), in the initial extraction. The authors have not found it necessary to prevent the extraction of silver by the addition of hydrochloric acid, since this is accomplished by hydroxylamine hydrochloride. Added quantities of silver up to 1 mg. carried through the complete procedure failed to affect the recovery of mercury.

The removal of free fats or fatty acids is necessary because of their effect on the extraction agent, but their removal, as also shown by Laug and Nelson (*6*), does not result in losses of mercury. Experience has demonstrated that some fatty material is dissolved by the chloroform in the initial extraction step and that this may be carried over into the acid-thiosulfate mixture. A considerable portion of this fat is removed when the acid-thiosulfate mixture is washed with clear chloroform and the greater portion of the remainder is destroyed in the acid-permanganate boiling procedure used to break up the mercury-thiosulfate complex preparatory to the final colorimetric extraction. A slight yellow color remains in the aqueous layer (particularly when large samples have been employed), but this color does not appear to be extracted by the final extraction solution.

The use of the thiosulfate complexing medium permits a final extraction for colorimetric purposes at pH 0.5. This is beneficial in avoiding interference by other metals, particularly lead, zinc, and cadmium, which might prove harmful at pH 6, such as is used by Laug and Nelson (*6*), particularly if through error the acidity should be less than this value. Laug and Nelson avoid these possible interferences by purifying their iodide and buffer solutions, steps which are unnecessary if the method described above is used. The only elements that might be expected to give trouble under the conditions of extracting at relatively high acidity are copper, silver, and bismuth. The latter two, however, are not extracted in the presence of chloride ion (obtained from the hydroxylamine hydrochloride which is added in both the initial and final extraction steps), while the former remains in the chloroform layer when the initial extraction solution is shaken with the acid-thiosulfate solution. In the use of the latter the only precaution required is that the acid-thiosulfate solution should be made up fresh just before use; otherwise the thiosulfuric acid is decomposed with deposition of sulfur and consequent loss in mercury-complexing ability.

The lack of stability of the mercury-dithizone complex (*6*) is a decided disadvantage which has been overcome by the use of di-β-naphthylthiocarbazone. The complex of the latter reagent with mercury is stable and no loss in color has been observed after 1 hour of exposure of the solutions to strong artificial light. No effort is made to protect the solutions of the mercury-di-β-naphthylthiocarbazone complex prior to their final introduction into the photometer, although they are not allowed to stand in strong sunlight.

The di-β-naphthylthiocarbazone was prepared by one of the authors, by a method described elsewhere (*5*). The reagent may be obtained from Eastman Kodak Corporation, but the product so available at present must be purified, since its molecular extinction coefficient (ε) at 645 mμ was found to be approximately 10,000 as compared to that of 42,000 which characterizes the twice repurified product made by the Scott and Hubbard method and which was used in this work (*5*). After one purification, the Eastman product had an extinction coefficient of 25,000. Apparently the method originally used by Hubbard (*4*), which was a modification of Suprunovich's method (*9*), gave a somewhat purer product than that made subsequently (*5*), since an extinction coefficient of 45,700 was obtained for it. This apparently superior method, however, is impractical because of its very low yield. In Figure 2 is shown a transmission curve for the twice purified product made by the Hubbard and Scott method (*5*). This curve was obtained with the Beckman spectrophotometer, the readings being made at 10-mμ intervals until the peak of absorption was near, when they were made at 5-mμ intervals. By reason of the use of the Beckman instrument, this curve is more accurate than that shown previously (*4*).

Finally, the authors have attempted to employ the spectrograph for the determination of mercury in biological material. The spectrographic sensitivity was found to be satisfactory only following isolation of the mercury and reduction of the resultant solution to a volume of 0.5 or 1 ml. These procedures always resulted in some loss of mercury and therefore the spectrographic method was abandoned in favor of the purely chemical method described above.

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NOTES ON ANALYTICAL PROCEDURES

A Versatile Electronic Relay

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An electronic relay is described which is variable in sensitivity, requires at most only a few microamperes of contact current, can be adjusted to the inherent resistance of the regulator circuit, and incorporates a photocell for light activation of the relay.

A NUMBER of electronic relay circuits have been described in the literature (*1*, *3–6*) during the past few years. The general trend has been toward the development of a relay requiring regulator contact current in the order of a few microamperes, so as to prevent deterioration of the mercury-platinum or the bimetallic strip regulator contacts. In using these relays, it is necessary that the regulator elements be well insulated and their connecting leads short and with good insulation, since any reduction in the necessarily high open circuit resistance, due to high humidity or insulation leakage, may prevent normal use of the relays. Moreover, these relays are usually of fixed types, each serving only one purpose, so that, for different uses, either several specific types of relays must be present in the laboratory or circuit changes in the existing instruments must be made.

The relay described in this paper offers the following features not found as a group in the usual electronic relay:

By means of a six-point selector switch in conjunction with a potentiometer, the relay can be adjusted rapidly for use with any type of regulator having contact and connecting wire lead resistances from approximately 0 ohm to 250 megohms.

It is provided with a socket to receive an emission-type photocell for light activation of the relay, to operate either alone or in conjunction with the usual type of regulator.

The relay will open or close the 117-volt alternating current control contacts either upon opening or closing of the regulator contacts, or with increase, decrease, or interruptions in the light striking the photocell.

Using the low resistance range, the regulator contact current does not exceed a few microamperes and is as low as a fraction of a microampere for photocell operation or in using the highest resistance range.

Series resistances are provided to protect the operator from accidental shock by body contact with the regulator terminals.

RELAY CIRCUIT

The relay circuit shown in Figure 1 illustrates the use of a type 2050 gas tetrode (interchangeable with type 2051), operating on alternate half waves of the alternating current cycle, in a conventional circuit (*2*) modified for the purpose. This type of tube was chosen for its high current-carrying capacity and for the triggering action of the grid where, when the critical grid-firing voltage is reached, the tube conducts to its maximum capacity. The necessary voltages for plate and grid operation are obtained from the voltage divider, R_1 to R_4, with the voltage developed across R_1 and R_2 supplying the plate a voltage positive with respect to the cathode, and the voltage across R_3 and R_4 negative with respect to the cathode on the same half cycle for grid control. R_3 gives a minimum negative grid bias voltage just in excess of cutoff, while R_4 allows for an additional grid bias voltage, variable to the grid through potentiometer R_5. The use of resistors R_8 to R_{13} allows for the ranges of sensitivity desired for operation of the relay.

With S_2 in position 6 and the control on R_5 moved all the way up (minimum setting), the relay will operate with contact resistances across T_R of as much as 250 megohms, while with S_2 in position 1 and the control of R_5 all the way down (maximum setting) practically a zero resistance is necessary. On adjusting S_2 to intermediate contact points and varying R_5 for each position of S_2, a complete range in between is available.

The plate circuit relay, R_E, is of 1500 ohms' resistance requiring approximately 8 ma. for operation. Under the conditions of available plate voltage, a relay requiring up to 35 ma. and of lower resistance could have been used. However, under these conditions and especially if the circuit is to be turned off and on frequently, a switch should be inserted in the plate circuit to provide a minimum delay of 10 seconds after turning on S_1 before applying the voltage to the plate of the tube. This is recommended by the manufacturer of the tube, since turning on the heater and plate voltages at the same time may result in reduced tube life. The authors have not experienced this difficulty in the use of the instrument as described. The holding condenser, C, is necessary to prevent chattering of the plate circuit relay, since the operation of the relay depends upon half-wave plate rectification. The plate circuit relay has a set of single-pole single-throw contacts connected to a pilot lamp to indicate operation and a set of single-pole double-throw contacts to deliver up to 6 amperes at 117 volts alternating current to a dual outlet receptacle, so that "normally open" or "normally closed" relay service is available for operation of the desired control device. If a greater load is to be operated, a heavy-duty alternating current relay can be placed in the control contact circuit or a plate circuit relay with suitable contacts can be substituted.

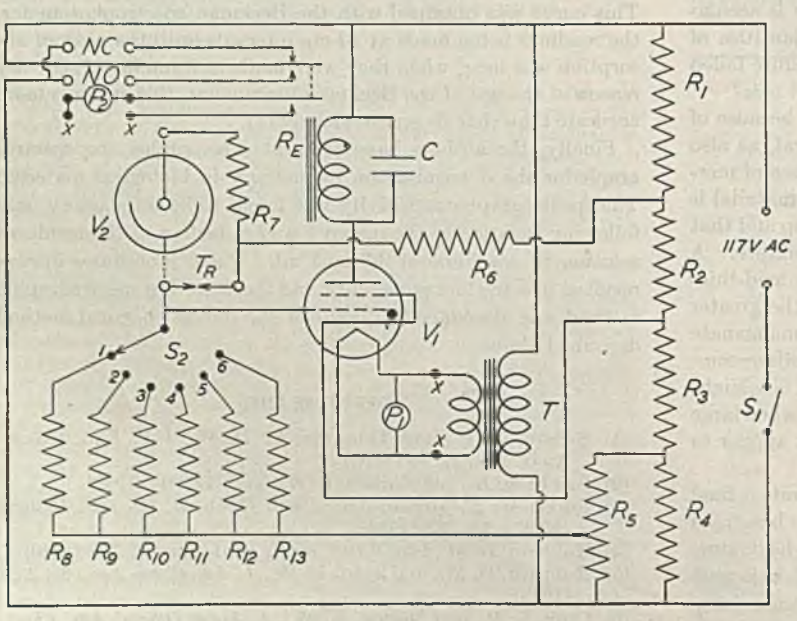

Figure 1. Circuit Diagram of Relay

V_1 = 2050 gas tetrode; V_2 = 868 gas photocell; T = midget filament transformer 117, 6.3-volt Thordarson T19F80; R_E = plate circuit relay; P_1, P_2 = 6.3-volt pilot lamps, Mazda No. 44, in Drake No. 20 leweled sockets; S_1 = midget toggle switch; S_2 = six-position Mallory selector switch No. 1316L; C = 10-μfd. electrolytic condenser, 50-volt DCWV; R_1 = 10,000 ohms; R_2 = 5000 ohms; R_3 = 900 ohms; R_4 = 1750 ohms; R_5 = wire-wound potentiometer of 10,000 ohms, Mallory No. M10MP; R_6 = 250,000 ohms; R_7 = 5 megohms; R_8 = 100,000 ohms; R_9 = 250,000 ohms; R_{10} = 500,000 ohms; R_{11} = 1 megohm; R_{12} = 5 megohms; R_{13} = 10 megohms. Resistors R_1 to R_4 are Brown Devil 10-watt wire-wound resistors. R_6 to R_{13} are 0.5-watt carbon resistors. T_R = thermoregulator, *NC* and *NO* are normally closed and normally open relay contacts. Pilot lamp P_2 indicates when relay is energized, while P_1 indicates continually while instrument is in use

The transformer, T, is a midget filament transformer to supply 6.3 volts to the heater of the 2050 tube. Resistor R_7 is a current-limiting resistor for the type 868 photocell. R_6 is a regulator contact protective resistance and should be approximately 250,000 ohms. Figure 2 is a photograph of the instrument.

BASIC OPERATION OF THE CIRCUIT

The circuit operates in the following manner. With the regulator terminals, T_R, open or the phototube dark (or at some predetermined light intensity depending on the setting of S_2 and R_5), the grid of the 2050 is at a voltage more negative than the critical grid firing voltage as determined by R_3 and the setting of R_5. When contact T_R is closed, or the photocell illuminated (or the illumination increased), the grid is brought to a potential less negative than the cutoff voltage, causing the tube to fire and energize the plate circuit relay.

OPERATION OF THE RELAY

After connecting the relay to a thermoregulator or similar activating mechanism and with contacts T_R open, switch S_2 can be moved progressively from contact 1 toward contact 6 and if the relay operates, owing to leakage across the wire leads from the regulator, switch S_2 can be backed off one position (or the setting of R_5 lowered) until the plate circuit relay does not become energized except when contacts T_R are closed. Actually for most uses of the relay, except under conditions of very high humidity, or when using the photocell, switch S_2 can be left permanently in positions 3 or 4. For excitation of the relay using the photocell, the procedure described previously can be employed. When the position of S_2 is found where the relay operates for any given light intensity on the photocell, backing off S_2 one step will cause it to cease operation. A position of R_5 can then be found where slight movement one way will cause the relay to operate, and movement in the opposite direction will cause it to be nonenergized. If R_5 is now left in the position where the plate circuit relay does not operate, a slight increase in the light will cause it to be energized and with a decrease it will again be inoperative. The instrument is made very flexible in its use by simply adjusting S_2 and R_5 as outlined.

The relay is easy to assemble, requires no preliminary adjustments, and should cost approximately $13.50 for all parts. If photocell operation of the relay is not desired, V_2 and R_7 can be omitted, reducing the total cost to $10. The present relay has been in almost continuous use without any attention for more than two years, controlling the temperature of a constant-humidity chamber using a toluene-mercury-platinum thermoregulator.

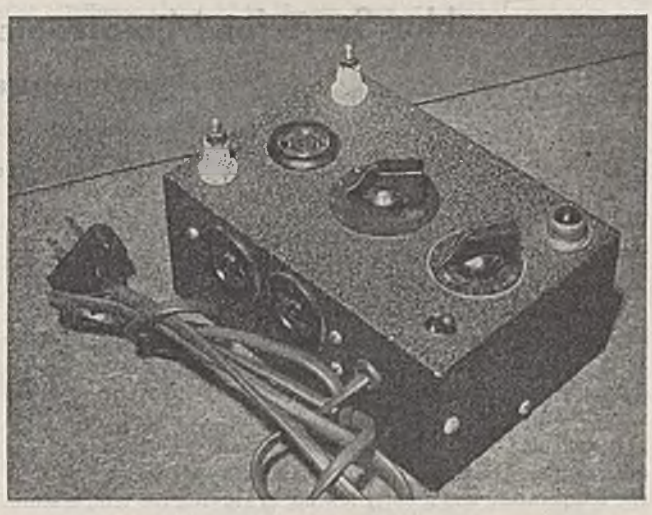

Figure 2. Photograph of Relay

Through-panel insulators for thermoregulator T_R are at far end of panel with photocell socket V_2 between them. Selector switch S_2 is in center and control to R_5 below. To left of control to R_5 is switch S_1; P_1 is to right. Pilot lamp P_2 is not visible from this view. Dual outlets to *NO* and *NC* are on left side of cabinet. Entire assembly is a $2^5/_8 \times 4^1/_8 \times 6^1/_8$ inch cabinet, black crackle finish

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Kettle for Measuring Small Residues in Low-Temperature Fractional Distillation

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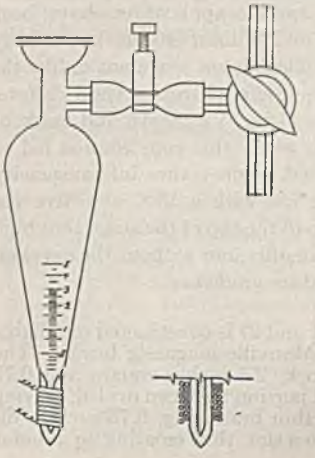
Continental Oil Company, Ponca City, Okla.

SOME samples for low-temperature fractional analyses require the measurement of very small liquid residues, when under the conditions of the analysis, it is impossible to vaporize the residue and measure it as a gas. If it is necessary to pour the residue from the kettle before measuring it, very large samples must be taken, so that the liquid remaining in the kettle will not be a large part of the total residue. A kettle in which it is possible to measure accurately small residues is advantageous, since time is saved by the use of samples of moderate size. Two types of sample which contain a very small proportion of heavy material are the effluent from a polymerization plant and the raw gasoline stream from a natural gasoline plant which recovers a large amount of propane and butane.

The figure shows a kettle made from the lower end of a California-type 100-ml. graduated centrifuge tube. The heating coil is wound upon a 19-mm. piece of capillary tube, which is fused to the end of the centrifuge tube. The volume of the capillary is determined by adding liquid from a buret to the centrifuge tube; if the buret reads 1.1 ml. and the centrifuge tube reads 1.0 ml., the volume of the capillary is 0.1 ml. The heater consists of 23 cm. of No. 28 resistance wire, which is wound between two layers of closely wound asbestos or glass string. The wire may be threaded through a Fiberglas sleeve before winding. The string and the wire are fixed by the liberal application of water glass.

The upper section of the centrifuge tube is pulled off at about the 30-ml. mark, and an 18/9 female ball joint is sealed to the rounded end. The male part of the joint is sealed to the distilling tube of the low-temperature fractionating column. The sample is introduced through the capillary connection which is sealed to the stem of the female joint. The three-way stopcock is attached to the capillary by means of a short piece of rubber tubing. A pinchclamp or a screwclamp on the rubber tubing helps to prevent leaks around the stopcock. The vertical arms of the cock are used to purge the line from the sample container. The kettle is immersed in liquid nitrogen contained in a Dewar flask during introduction of the sample.



After distillation is completed, the kettle is immersed in ice water, in order to condense vapor and cause the reflux liquid to leave the packing of the distilling tube and collect in the kettle. The kettle is then immersed in water at 60° F., and the volume of the residue is read.

Hot Stage for Microscopic Observations between Room Temperature and 350° C.

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THIS note describes a small furnace found useful in studying phase relations with the aid of microscopic observation between room temperature and about 350° C. The design problem is that of maintaining a temperature gradient of up to 100° C. per mm. in one direction (so that the sample can be at a high temperature with the microscope objective still at room temperature) but with substantially zero gradient in the plane perpendicular thereto, over an area of 2 sq. cm. Additional requirements are a means for rapid and accurate measurement of the temperature and a fairly low lag in varying the temperature.

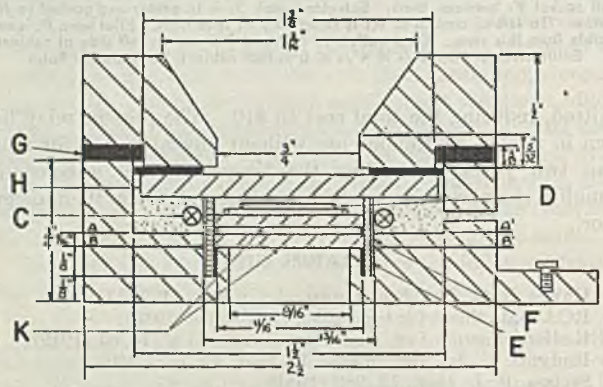

Figure 1. Cross Section of Microscope Hot Stage

C. Heating element
D. Capillary on wire coil
E. Brass ring
F. Mica strip
G. Asbestos disk
H. Pyrex disk
K. Glass disks

Commercially available heating stages are generally designed for biological applications and are not serviceable much above 50° C. Those few which can be heated to high temperatures are generally made of metal and therefore have a fairly high heat capacity which results in enormous temperature lag. The exterior of these stages becomes warm, with resultant inconvenience in manipulation. Metallic parts intended to distribute the heat uniformly usually undergo oxidation and deterioration with short use, and temperature inhomogeneity develops far greater than the usually claimed 1° above 200° C.

Custom-made hot stages for specific applications have been described (*1–4, 6, 11*). Wallace and Willard (*10*) devised a fairly simple, sturdy, and generally applicable hot stage not unlike the present design, which nevertheless suffered from several defects. The heated chamber was 2.5 cm. (1 inch) in depth and made of Alundum wound with Nichrome wire; this construction led to the development of severe vertical temperature inhomogeneity within the furnace proper. For use with a 10× objective the specimen had to be raised so close to the top of the stage that high temperatures were not attained readily, nor without the development of large horizontal temperature gradients.

The present furnace (Figures 1 and 2) is constructed of a lightweight porous fire brick (Johns-Manville magnesia brick). The bottom section consists of a block, 2.5 inches square and 0.75 inch high, from which the central portion has been drilled, leaving the terraces, *AA′* and *BB′*. A thin brass ring, 0.75 inch in diameter and $^5/_{16}$ inch high, fits into a slot, thus creating an annular space into which is inserted the heating element composed of a 1-foot length of No. 26 Nicrome resistance wire wound as a spiral. The heating element is wrapped around the brass ring fairly tightly and is separated from it by two strips of mica in order to prevent the development of hot spots. The brass ring, with winding, is then embedded in position with shredded asbestos paper. The leads to the heating element are brought out through holes drilled in the block, and secured to the binding posts as shown.

Two $^1/_{16}$-inch glass disks, separated by an air space, $^1/_{32}$-inch asbestos spacer, fit into the well created by the brass ring, leaving approximately $^1/_{16}$ inch from the top of the ring to the top glass disk. These glass disks serve to insulate the heated air chamber of the furnace from the condenser system of the microscope, as well as prevent too great a heat loss from the center of the main hot stage chamber. This is an effective technique, since the lower chamber is heated by the brass ring almost as effectively as is the upper chamber. The disks may be chipped from microscope slides—held under water while chipping to prevent cracking—or a circular glass cutter may be used.

The microscope objective is protected from the furnace by a Pyrex disk 0.125 inch thick, cut from a well-annealed plate. The latter condition is important if the furnace is to be used with a polarizing microscope, in order to prevent depolarization by the disk. The 0.125-inch disk is used rather than another dummy air space, as formed on the underside of the main hot stage chamber, because of its greater convenience when changing specimens. This disk is sufficiently thick to prevent large heat losses from the center of the heated air chamber—heat conduction from its periphery, where it makes contact with the asbestos insulation, probably accounts for much of the heat loss to the environment—but does not conduct so well as to serve as a source of heat for the air chamber. This was confirmed by using a pair of reversed thermocouples—one junction sealed to the glass disk and the other positioned in the center of the air space—and determining that the temperature of the underside of the disk was an average of 0.5° to 1.0° C. lower than the temperature of the air chamber.

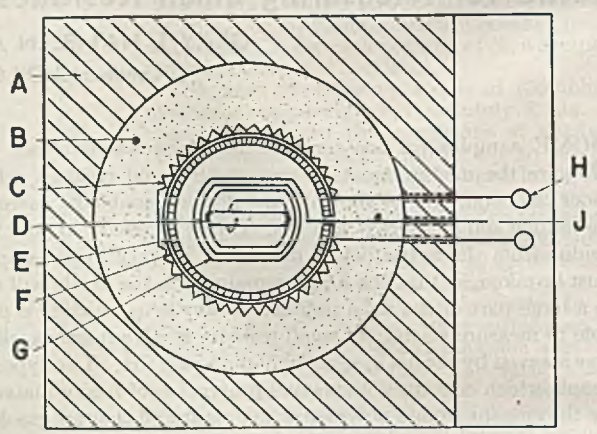

Figure 2. Section through Control Area of Hot Stage

A. Magnesia block
B. Asbestos paper
C. Heating element
D. Capillary
E. Brass ring
F. Mica strip
G. Thermocouple coil
H. Binding post
J. Thermocouple leads

A $^1/_{64}$-inch hole is drilled through the block and the brass ring to permit the entrance of a thermocouple for measuring the temperature within the ring. A thermocouple is preferred to a thermometer because of its much smaller heat capacity and its ability to measure a much wider range of temperature.

Copper-constantan thermocouple wire, No. 30 B. & S. gage, has been used successfully. Since the e.m.f. is 0.04 to 0.05 mv. per ° C., a Leeds & Northrup potentiometer and galvanometer, with a sensitivity of 0.015 microampere per mm., is satisfactory for measurements good to 0.3° C. If two or three loops of the thermocouple wire are left within the air space, conduction of heat along the wire is low enough so that standard calibration tables may be used. Otherwise, the calibration may run 2° to 3° C. lower than the reference tables at 300° C.

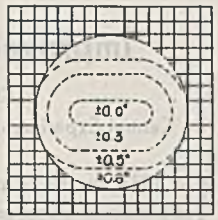

Figure 3. Temperature Difference between Center of Hot Stage and Other Parts

1 division = 1/16 inch. Determined at 250° C.

With this design, the air space within the brass ring can be maintained at temperatures up to 350° C. with the entire exterior of the block only faintly warm to the touch. Moreover, the heat capacity is sufficiently low so that a small change in heat input is reflected in a rapid adjustment of the temperature to its new value. The maximum rate of temperature rise compatible with maintenance of uniform temperature within the air space is 1.5° to 2.0° C. per minute. The temperature gradient under such circumstances is illustrated in Figure 3, which was determined by using two reversed thermocouple junctions and a galvanometer sensitive to 0.1° C.

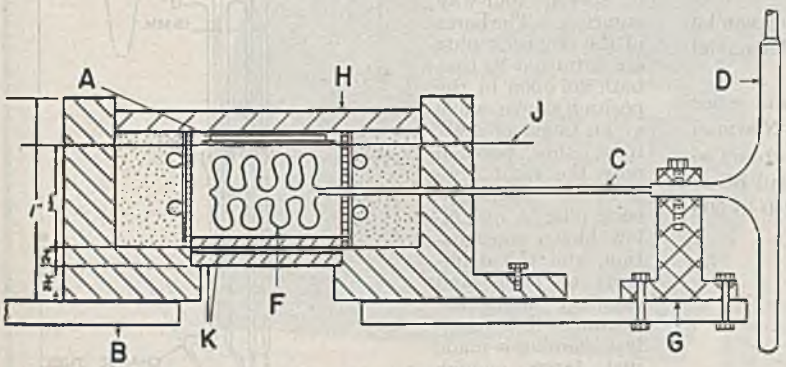

Figure 4. Cross Section of Modified Hot Stage

A. Microslide on wire coil
B. Microscope stage
C. Fan shaft
D. Air-driven rotor
E. Fan blade
G. Brass anchor block
H. Pyrex disk
J. Thermocouple lead
K. Glass disks

The temperature rise is controlled by means of a variac and a 12-ohm resistance, which is interposed in series between the furnace and the variac. The mean spontaneous rate of cooling with the heating element turned off is 20° C. per minute between 300° and 100° C., and 10° C. below 100° C.

The minimum distance from the microscope objective to the center of the heated space is approximately 4.2 mm., which with the usual design of microscope makes feasible the use of a 16-mm. (10×) objective, so that a magnification of the order of 100-power can be readily obtained. For intermittent observations the 0.125-inch Pyrex disk may be replaced by a 1/32-inch disk, permitting the use of a 20× objective. However, under such circumstances the heating rate should be below 0.7° to 1.0° C. per minute and the temperature should not exceed 200° to 250° C. in order to maintain the temperature homogeneity as indicated above.

The sample has to be mounted on a slide, cover slip, or other mount that can be contained entirely within the heated space. The field of view is adjusted entirely by moving the whole furnace about on the microscope stage. With a rotating stage, the furnace can be fastened to it, and moved with the adjustable spacers. The authors have been studying soap systems which must be protected from the air during heating and from vapor loss (*7*, *8*, *9*). It has proved convenient to contain such samples in sealed, flat capillaries about 12 to 15 mm. long, supported on a wire coil of the thermocouple wire, which in turn rests on the surface of the uppermost bottom glass cover of the furnace (see diagrams).

To test the accuracy of the hot stage, melting points were determined on the following:

Substance	Temperature, ° C. Observed	Reported
Tin	231.7 ± 0.3	231.9[a]
Urea	132.7 ± 0.3	132.6

[a] National Bureau of Standards sample.

In addition, phase changes in the system sodium nitrate–silver nitrate were determined to see if the points at the liquidus and solidus curves could be determined with accuracy. These results are:

Mole % Sodium Nitrate	Phase Change	Temperature, ° C. Observed	Reported (*5*)
0.00	Melting	208.8 ± 0.3	208.6
29.9	Melting	217.5 ± 0.3	217.5
	Freezing	235.2 ± 0.3	235.0
100.00	Melting	308.1 ± 0.3	308

In some cases, where the sample is spread over a more or less circular area, the temperature homogeneity may be insufficient for the most exacting work. To provide for such cases the authors have developed a modification of the furnace. The necessary changes in construction are indicated in Figure 4, and the temperature distribution obtained is shown in Figure 5.

In this modification the bottom section is 1 inch high. The brass ring is 9/16 inch high and is wrapped with two turns of coiled Nichrome wire instead of one, allowing for a heated space slightly greater than 0.5 inch in depth. Homogeneity is secured by the use of the stirrer blade, which is cut out from a piece of sheet copper, 9/16 by 5/8 inch. Eight blades are cut out as shown, and bent so as to circulate the air across the air space. The Pyrex disk should be cut to make a fairly tight fit in order to prevent leakage. The shaft, made of 1/32-inch Bessemer steel rod, is silver-soldered to the blade. The block and the brass ring are slotted to receive the shaft, so that the blade clears the top disk by at least 1/32 and preferably 1/16 inch. The shaft is driven by an air motor (Aero-Mix, Precision Scientific Co.) which is clamped by a brass block directly to the microscope stage, so that it is moved integrally with it. The specimen is again supported on a coil of the thermocouple wire, which is stiff enough to be suspended as shown.

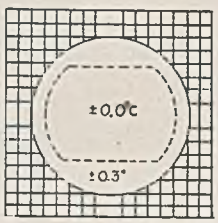

Figure 5. Temperature Distribution with Modified Hot Stage

1 division = 1/16 inch. Determined at 250° C.

ACKNOWLEDGMENT

The authors wish to express their appreciation to R. D. Vold for his interest during the development of this instrument.

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A Variable Pressure Manostat

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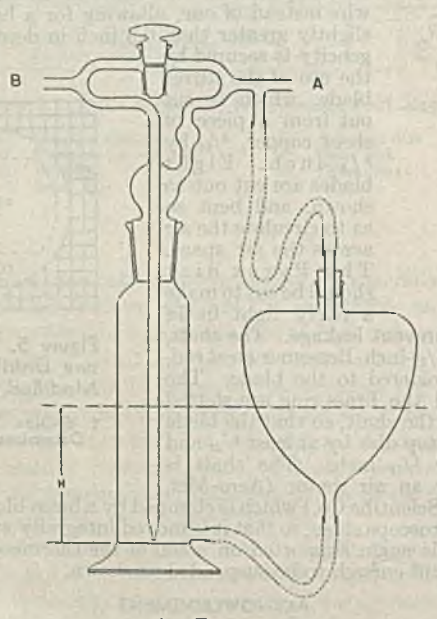
IT IS often convenient and sometimes necessary to reproduce or vary the pressure on a given system. The diagram shows an arrangement by which pressures may readily be set at any desired value or varied continuously, between limits determined by the efficiency of the pump and the height of the manostat, without removing the manostat from the vacuum line or interrupting the progress of the distillation.

Most vacuum distillations are conducted within the range from 1 to 250 mm. Any pressure within this range can easily be obtained by using a regulator of the Newman type (*1*) and inserting into the system a reservoir of mercury. Use of ethyl phthalate limits the range but makes possible more delicate setting. The height, *H*, of the liquid in the manostat can be changed manually during a distillation merely by adjustment of the reservoir (see diagram). A stopcock placed below the reservoir may be used to assure a constant head after setting. The entire assembly can be blown to order, but it is possible to make a very creditable model from a drying column.

Pressures above 250 mm. can be obtained by placing in series with the manostat described above two ordinary Newman regulators filled to the 250-mm. level. If the stopcocks are set so that both these regulators are by-passed, the range will be as stated above. With one tube cut in the range will be 250 to 500 mm.; with both, 500 to 750 mm.



A. To pump
B. To system

In the authors' opinion such an apparatus provides a more inexpensive and convenient method for checking boiling points at the pressures recorded in the literature than any heretofore described. The manostat has proved especially useful in the fractional distillation of mixtures when it is advantageous to distill the various components under successively lower pressures.

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Improved Adsorption Vessel

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Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

IN THE study of metal-oxide catalysts such as used in the Fischer-Tropsch process by low-temperature adsorption isotherms, it is desirable to reduce the catalyst in the adsorption vessel and to determine the weight loss upon reduction. The adsorption vessel shown in Figure 1 has proved convenient in such studies. It is small and light enough to be weighed in an analytical balance.

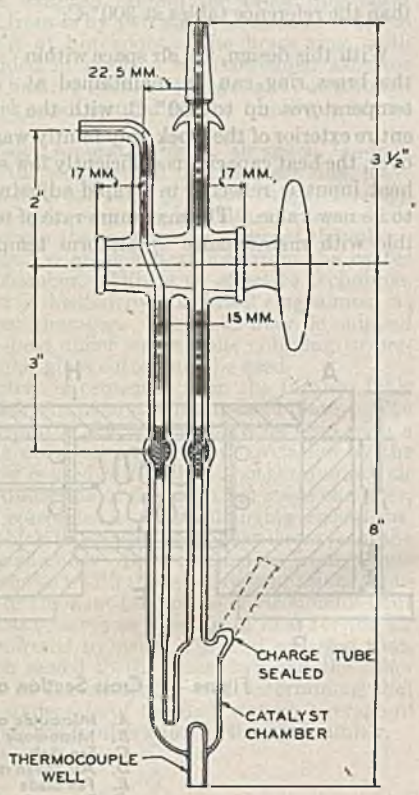

Figure 1

The absorption vessel consists of a catalyst chamber and a special four-way stopcock. The bores of the stopcock plug are arranged so that both are open in the position shown, while at an angle of 180° from this position only the right bore is open. The stopcock plug is of hollow blown construction, and the diameters of bores and capillary tubing are 2 mm. The catalyst chamber is made just large enough to accommodate the sample required, usually 1 to 2 cc. The catalyst chamber is provided with a tube for charging and a thermocouple well. The tubes leading to the stopcock contain loosely packed wads of glass wool to prevent the catalyst from blowing out of the chamber. The adsorption vessel is connected to the adsorption or reduction systems by a 10/30 capillary ground-glass joint.

With the four-way stopcock the sample can be connected to the system for adsorption or evacuation with one bore open, and with both bores open a stream of hydrogen can be passed over the catalysts. The sample of catalyst usually is weighed in the adsorption vessel before the charge tube is sealed. After sealing all weighings are performed with the vessel evacuated. Fresh samples are evacuated for an hour at 125° C. to remove water and other vapors that are held physically. The catalyst chamber is placed in a furnace in a horizontal position to avoid heating the stopcock.

Usually nitrogen adsorption isotherms at −195° C. were determined on the sample before and after reduction, and in some instances several isotherms were run during the course of reduction. With this adsorption vessel it also will be possible to study the effects of treatment of the catalyst with gases other than hydrogen, such as synthesis gas or carbon monoxide, on the surface area and pore structure, and to determine the weight loss of the adsorbent upon evacuation.

ACKNOWLEDGMENT

Acknowledgment is made to Martin Michael for preparation of the drawing. The special stopcock was made by Eck & Krebs.

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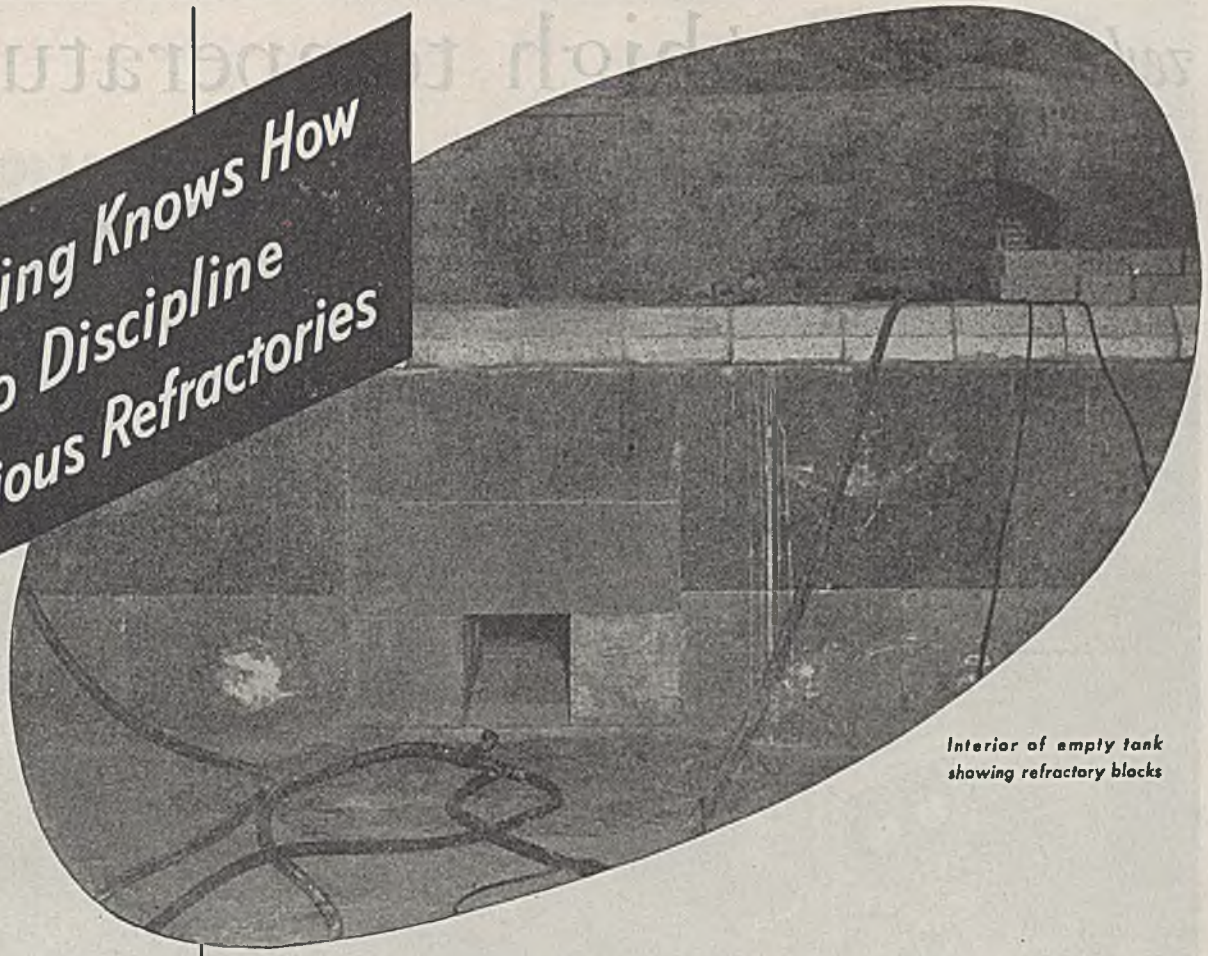
Corning Knows How To Discipline Fractious Refractories



Interior of empty tank showing refractory blocks

• A glass plant could not get along without refractories. But sometimes it is pretty hard to get along with them.

One of the major problems in glass making has always been to develop a suitable material to contain molten glass at high temperatures. The materials used are of the type commonly called refractories and all have various degrees of solubility in the glass thereby introducing undesirable impurities that cause defects known as stones, knots and cords.

That is why selection of proper refractories at Corning is entrusted to a Glass Technology Department. This department tests all kinds of refractories, specifies the proper type for glasses of different composition and checks performance in the many different tanks and furnaces.

Maintaining its own Pot and Clay Department, Glass Technology frequently makes its own refractories. One of its outstanding achievements has been the development of a special block for the melting of "Pyrex" Brand Chemical Glass and other glasses requiring extremely high temperatures. This new block is very effective in safeguarding the quality of "Pyrex" Brand Ware by minimizing undesirable impurities.

The Glass Technology Department typifies the controls exercised throughout Corning from research laboratories to shipping rooms. Quality is protected every step of the way. The familiar "Pyrex" trade-mark is your assurance of dependability. Consult your Laboratory Supply Dealer.

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Current Developments in INSTRUMENTATION IN ANALYSIS

Discussed by Ralph H. Müller

We record a few random thoughts on analytical spectroscopy this time. They are inspired primarily by two excellent papers, but also by some opinions which we have held for some time and, in which, circumstances permit us to do nothing more than talk about them.

Analytical Spectroscopy

It has been recognized for some time that in routine, repetitive spectrographic analysis, the photographic technique, with its attendant complications and the need for a good densitometer, will soon be replaced by more direct methods. By no means the first attempt in this direction is the work of G. A. Nahstoll and F. R. Bryan of the Ford Motor Co., who report on "An Application of Multiplier Phototubes to the Spectrochemical Analysis of Magnesium Alloy" [*J. Optical Soc. Am.*, **35**, 646 (1945)].

An RCA 1P28 photomultiplier tube is used to scan a reference line of the matrix element. Another identical tube is suitably located to intercept an appropriate line of the desired constituent. The ratio of phototube outputs is measured with a vacuum tube voltmeter, the scale of which is calibrated directly in concentration units. The authors have indicated some of the difficulties; in particular, the need for integration over a period of time to compensate for source fluctuations. Nevertheless, the arrangement has served their immediate purpose and for determining Al, Si, Cu, Ni, Zn, Mn, Pb, and Fe they state that one operator is able to make 80 determinations per hour, and two operators can handle 100.

The second paper is the most impressive account we have ever seen on this subject. J. L. Sanderson, V. J. Caldecourt,, and E. W. Peterson of the Dow Chemical Co. describe "A Photoelectric Instrument for Direct Spectrochemical Analysis" [*J. Optical Soc. Am.*, **35**, 681 (1945)]. Here, the same problem is studied exhaustively and developed into a completely mechanized installation handling 4000 samples per month or approximately 20,000 determinations. It has been in operation for one year and uses nontechnical personnel.

As many as ten photomultiplier tubes, along with a monitoring tube, are mounted behind exit slits in a grating spectrograph. Each tube receives a carefully selected line of the desired constituent. The slit system will admit a line plus background radiation, or in a magnetically controlled second position, the background alone. In the first of these two positions, the tube charges a capacitor at a rate depending upon the intensity of line and background. In the second position, the same capacitor is discharged by the same tube, now illuminated by background only. The charging and discharging cycles are each of 1-second duration, and the total sample-sparking time is 20 seconds. At the end of this period, the capacitor is discharged through a resistor. The same process has been taking place in the monitoring tube. From the exponential nature of the RC combination, the time required for discharge to some convenient reference voltage is proportional to the logarithm of the original light intensity. The difference in time required for measuring and monitoring systems to discharge is automatically recorded on a strip chart. All the other determinations are proceeding simultaneously using duplicate parts. This ingenious scheme provides integration which minimizes source fluctuations and also corrects for background. In 40 seconds, the results can be read from the chart lines with the aid of photoprojected calibration scales. For small amounts of constituents, the precision is comparable to the photographic process; for larger amounts, it is somewhat better. Technical vision and competence, adequate funds, and sympathetic research administration seem to be an invincible combination! We hope you will read this paper for full detail.

Iconoscope and Orthicon

As to random thoughts—we would like to nominate the iconoscope and orthicon for the consideration of spectrographers. These image-forming tubes should be very useful. Before the war, with the help of able colleagues, we whirled a spectrum across a stationary slit, behind which a photocell was placed. A video amplifier presented the information to a cathode-ray oscillograph. Proper sweep synchronization provided a horizontal wave-length axis and further refinements furnished a more or less equal energy response to different wave lengths. The result was a fairly good spectrophotometer, or a densitometer if we were scanning a spectrogram with white light, and a combined spectrograph-densitometer. The entire pattern was repeated on the screen several times per second. It was obvious that the mechanical scanning should be replaced by an iconoscope, wherein the spectrum is projected on the mosaic and then scanned electronically. The speed and resolution would be much greater. College research budgets have a habit of folding up at such junctures. We hope some one else will do it. It is worthy of note that the iconoscope mosaic has storage or integrating properties.

Analytical Spectroscopy without a Spectroscope?

These are technical improvements and applications of well-known principles. We now venture to raise the question, "Is 'analytical spectroscopy without a spectroscope' a completely ambiguous statement?" We think it is not. There are several phenomena which are worthy of careful study and which may ultimately furnish the equivalent information. The most important of these, we believe, is a detailed study of the electrical and optical behavior of arcs.

The electrical excitation of atoms in the vapor of an arc is a stepwise phenomenon, governed by well-known quantum principles. Under ideal conditions, critical potentials are easily determined for the various energy levels and these are unmistakably related to the optical frequencies which follow such transitions. The large mass of data which has been accumulated on critical potentials was obtained under conditions of constant low pressure of metal vapor and with elaborate means for accelerating electrons through it. By comparison, an open arc is a very ragged and erratic affair. Nevertheless it should be possible to learn a great deal by scanning an A.C. arc with a photocell and observing the light emission at microsecond intervals during, let us say, the first quarter or fifth of an excitation cycle. Electronic techniques for such short-term scanning are abundant. By one of them, it is possible to switch or "gate" the measuring amplifiers to any specified time interval after the beginning of a cycle. It is equally feasible to render the scanning process insensitive to the bulk constituents of the arc, by operating another arc in series, or at least in phase. The optical responses common to both are then fed to a coincidence circuit which initiates proper blanking of the measuring amplifier. We make no specific claims for the utility of what may be found in such investigations, but we do know that the technique for the "leisurely" examination of an arc during the first few thousandths of a second of its life is at hand. We would be surprised if it were not at least interesting.

We hasten, at this point, to meet one valid objection to these suggestions. One might justly ask, "Is it not true, that after all the technical difficulties are surmounted, the critical potential data will be disappointingly meager, compared with the wealth of spectral lines which are observable in the conventional spectroscopic technique?" While intercombination terms can be detected, especially with the Franck and Einsporn method, it is true that the successive stages of critical impacts which can be revealed are meager compared with the many optical frequencies to which they give rise, directly or indirectly. From the analyst's point of view, this may turn out to be of little consequence, because he discards most of the spectrum in any case, and derives the essential information from one or two characteristic lines. By the same token, there is little of interest in these suggestions to the spectroscopist concerned only with hyperfine structure, Zeeman patterns, or isotope shifts.

Instrumentation

Mass Spectrograph

One cannot dismiss the subject of critical potentials, and the need for re-examining them with the newer electronic techniques, without mentioning the mass spectrograph. Lest it be considered presumptuous to criticize a half-century of development in this field, we know that the wartime services of the mass spectrograph, especially in the synthetic rubber field, have given it a degree of immunity sufficient to withstand any crude, though well intended reforms. It must be admitted that when complex organic molecules are admitted to the system and bombarded by electrons, we must look hopefully at the exit slit for the debris which will be hustled there by electrostatic and magnetic deflection, and by empirical calibration, relate the fragments to that which was originally placed in the hopper. With monatomic or diatomic species the whole thing is straightforward, but when we deal with large molecules one cannot escape the feeling that it is similar to training a howitzer on a cathedral and then calling in an architect to view the rubble and to describe the original structure. Therefore, we ask again, is it worth while to examine the original processes, the bombardment of the molecules, in great detail? We are aware that the early studies on even fairly simple molecules showed critical potentials which were notoriously monotonous and uninformative. Is there more to be found by better techniques? Perhaps we may be told by someone who knows better, that quantum mechanical considerations require that a molecule of any considerable complexity simply acquires a minimum amount of energy from impacting electrons, with no sharp or specific requirements, and then, in a frenzy, flies apart into assorted fragments. We would really like to know what goes on.

Further inquiry into the phenomenon of self-absorption should be profitable. Atoms in the vapor of an arc are in excited states, several of which are opaque to monochromatic radiation of the correct frequency. It is conceivable that this absorption could be measured by light from another arc. In this case the analyzing beam would be chopped or interrupted at high frequency and then differentially measured, after passage through the arc, by a photocell and tuned amplifier.

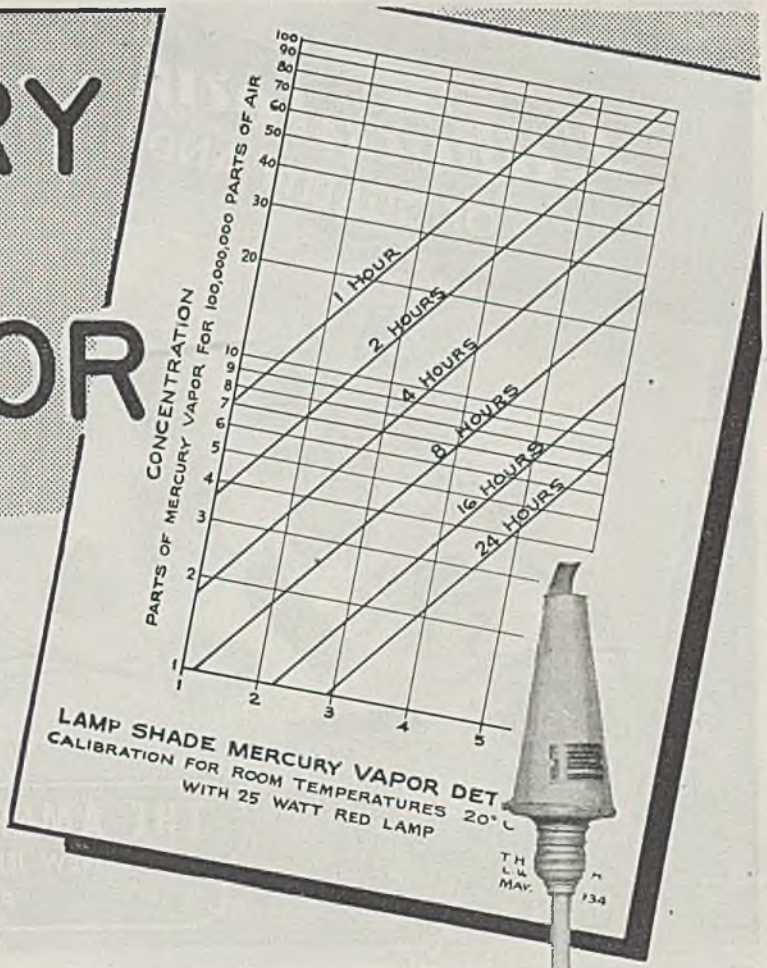
There seems to be some promise in the measurement of the *velocity* of photoelectrons. According to Einstein's law $Ve = h\nu - h\nu_0$, the velocity of a photoelectron is directly proportional to the frequency and independent of the intensity. The photoelectric cutoff for monochromatic radiation is particularly sharp and distinct for central-cathode cells, because they exhibit saturation at zero applied potential. All this has been known for many years, but recently RCA investigators have reported some success in applying the principle in this manner.

Most Instrumental Methods of Analysis By-Products?

These random reflections pose a more general question, "Is it not true that most of our instrumental methods of analysis have been by-products of some other problem or technique?" That is debatable in the case of spectroscopy, because Bunsen and Kirchoff discovered two new alkali metals soon after they devised the spectroscope; but the many exciting applications to physics and astronomy obscured this use of the instrument for several decades. Most of our electrometric techniques follow the pattern in which the analytically useful aspects were gradually recognized, but their wide acceptance required many years. Polarography would seem to be another exception, in that its analytical significance was quickly perceived by its inventor. Is it not high time that we begin an intensive re-examination of all physical and chemical phenomena for their analytical possibilities and with the latest techniques?

After which—we extend a broad apology to manufacturers of spectrographs who are constantly improving their instruments and are providing us with precision tools. To the spectrographer we bow twice, because his unremitting labor and care have brought analytical spectroscopy to the point where it performs a large part of the world's analysis—with speed and precision. But there is the future—and we were just wondering, that's all.

MERCURY VAPOR DETECTOR

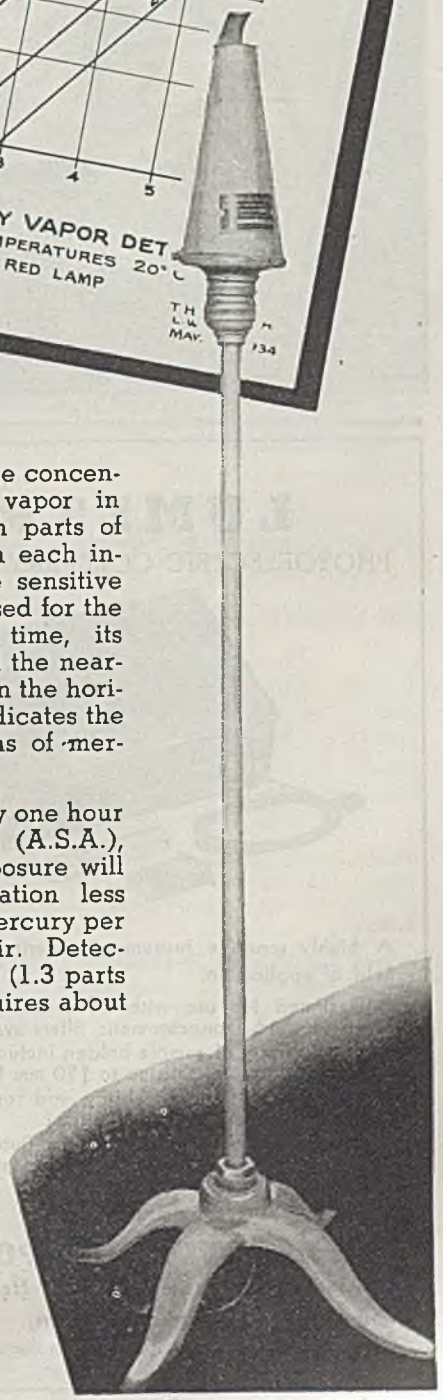


Mercury vapor from spilled droplets of mercury hidden in crevices throughout the laboratory may over a period of time reach the toxic concentration point and be injurious to the health of the laboratory workers. The toxic limit for continual breathing as established by the American Standards Association (Report Z 37.8–1943) is 1.3 parts of mercury vapor in 100 million parts of air by volume. By determining the concentration of mercury vapor in the air precautions can be taken to keep the mercury-vapor concentration below the harmful limit and safeguard the health of workers exposed to the vapor.

No. 20150 Mercury-Vapor Detector utilizes a chemical method for detecting as little as seven parts of mercury in 100 million parts of air in one hour. In six hours the apparatus will indicate that the toxic limit has been reached. The apparatus consists of a truncated cone which acts as an air chimney mounted on a suitable stand. A reasonably constant temperature and an upward flow of air through the cone are provided by a 25-watt red Mazda lamp in the base of the cone. Fastened to the top of this chimney is a curved paper holder, past which the upward air draft must flow. The holder accommodates strips of selenium-sulfide-sensitized paper 7/8 inch wide by 2 inches long. A cross-draft eliminator, in the form of a cylinder mounted around the holder, is provided to prevent air other than that from the chimney from striking the paper.

A calibrated color chart with a horizontal scale of six shades of gray for matching with the exposed paper, and a vertical scale for indicating the concentration of mercury vapor in parts per 100 million parts of air are provided with each instrument. When the sensitive paper has been exposed for the required length of time, its color is matched with the nearest of the six shades on the horizontal scale which indicates the various concentrations of mercury vapor.

An exposure of only one hour is recommended (A.S.A.), though this short exposure will not detect concentration less than seven parts of mercury per 100 million parts of air. Detection of the toxic limit (1.3 parts per 100 million) requires about six hours.



No. 20150 Mercury-Vapor Detector is designed for operation on 115 volts. Price..... $50.00

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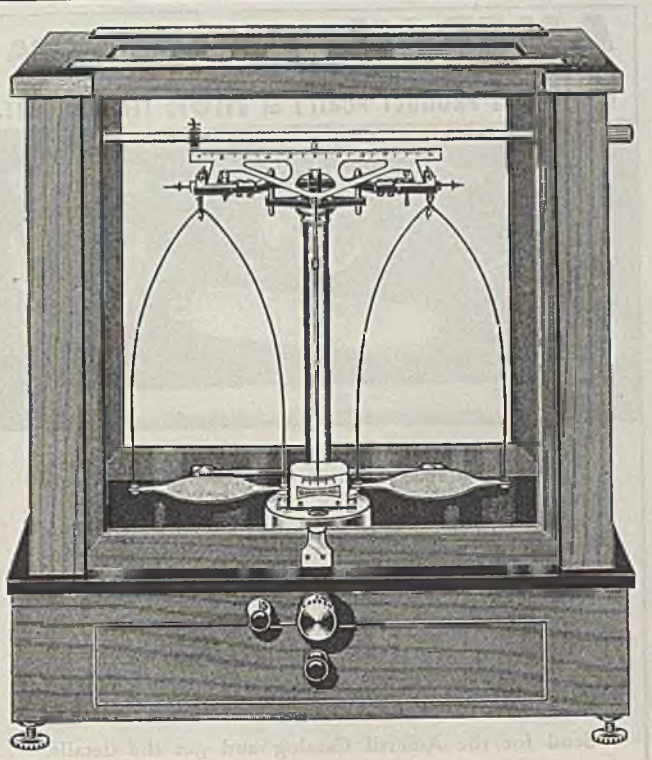

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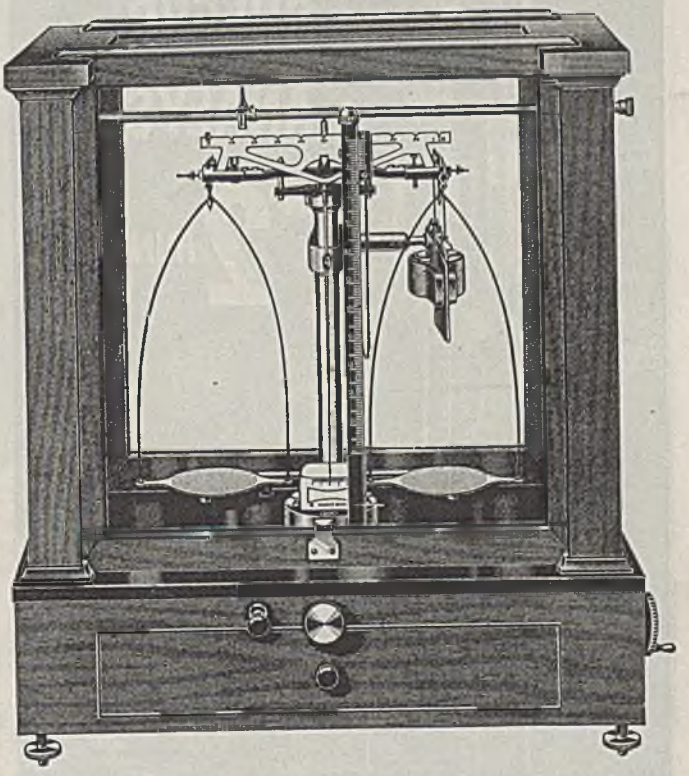
Capacity—200 grams on each pan
Sensitivity—1/20 Mg. with full load



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These SeKo Analytical Balances are well suited to work in industrial and educational laboratories which require high accuracy coupled with moderate price. They are ruggedly built and attractive in appearance.

Specifications

Capacity—200 Gms. on each pan

Sensitivity—1/20 Mg. with full load

Beam—6½ in. (16.5 cm.) long, sawed from special aluminum of great tensile strength and uniform density.

Knife Edges—Agate, large triangular shape.

Bearings—Agate planes. All knife edges are entirely free from the bearings, when the balance is arrested.

Releasing Mechanism—Fallaway type, with three point suspension for beam. Controlled by an eccentric shaft which is positive and effective.

Pans—Aluminum, 2½ in. (6.4 cm. diameter)

Bows—Nickel silver, 4⅛ in. wide × 8 in. high inside. (10.5 × 20 cm.) pan Arrest—independent, with locking stop.

Index Plate—White field with black graduations. Of the double type. Pointer swings above graduations, thus avoiding parallax.

Column—Brass, polished and acid resisting lacquered.

Case—Dimensions overall, 16½ in. long, 9½ in. deep, 18½ in. high. (42 × 24 × 48 cm.). Seasoned polished mahogany, with glass sides and top, front sliding door counterpoised, rear door sliding and removable. With circular allway level and leveling screws. Black glass base plate.

1820—SeKo ANALYTICAL BALANCE, Rider Type. Beam graduated in black, 50 divisions each side from center. Used with 5 Mg. Rider, each division equivalent to 1/10 Mg **$162.50**

1823—SeKo ANALYTICAL BALANCE, with Chain Device and Channel Notched Beam. Specifications same as for No. 1820 but with chain device and notched beam so that no loose weights are required for weighings from 1/10 Mg to 1.1 Gm **$237.50**

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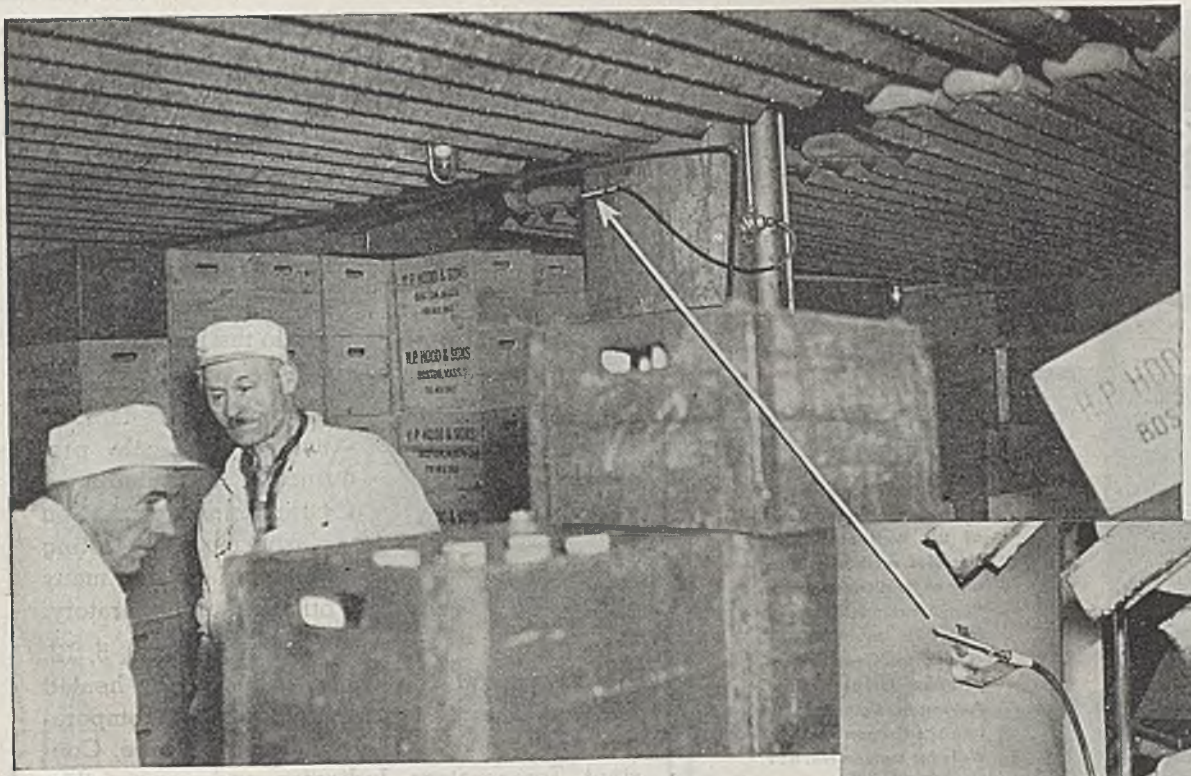
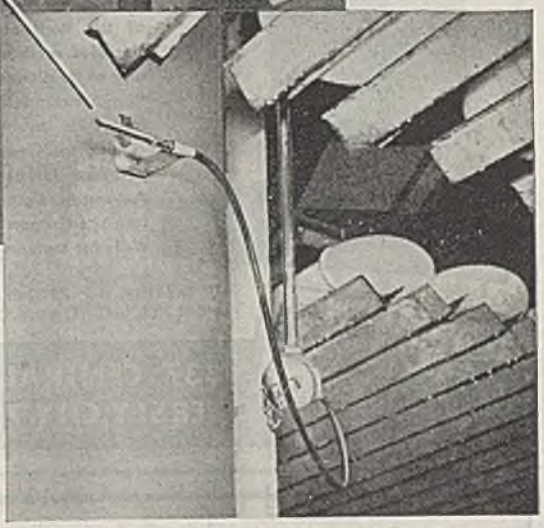


Milk chest (cold storage room) from which H. P. Hood & Sons, Boston, ship their A and B milks. Chest temperature is remotely recorded by Micromax instrument; fixture indicated by arrow is Recorder's temperature-detecting Thermohm.



How MICROMAX Saves Steps In H. P. Hood & Sons Power Plant

"It saves us a thousand steps an hour," says the chief engineer of H. P. Hood & Sons, referring to the Micromax Recorder which charts temperatures of storage chests in the milk plant.

Formerly, when mercury or spirit thermometers were used for temperature checks, much time and effort went into the continuous trek from chest to chest. Even so, engineers had only an intermittent guide to correct refrigeration.

Now, the Micromax Recorder, located right in the power plant, gives an accurate record for all chests, so that off-temperature is a thing of the past. Thus stocks are safer, because temperature can be kept more strictly within limits. Fuel is saved, since there is no longer any need to over-refrigerate.

The Recorder used is a multiple point instrument, capable of recording as many as 16 readings, for near or distant chests. The Thermohms (electrical resistance thermometers) which do the detecting, are ideal for "low" temperatures, retaining sensitivity and requiring minimum maintenance under any refrigerating conditions. If damaged, a Thermohm or its leadwire can be replaced without affecting the instrument's calibration.

Bring your refrigerating-temperature problem to the attention of our engineers, or if you prefer, request Catalog N-33C.

"Hood" power-plant engineer logs temperatures of milk chests, reading the multiple point record kept by the Micromax Recorder. Installed in the plant's powerhouse, Recorder is conveniently located within 25 ft. of valves, making prompt, exact control possible.

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