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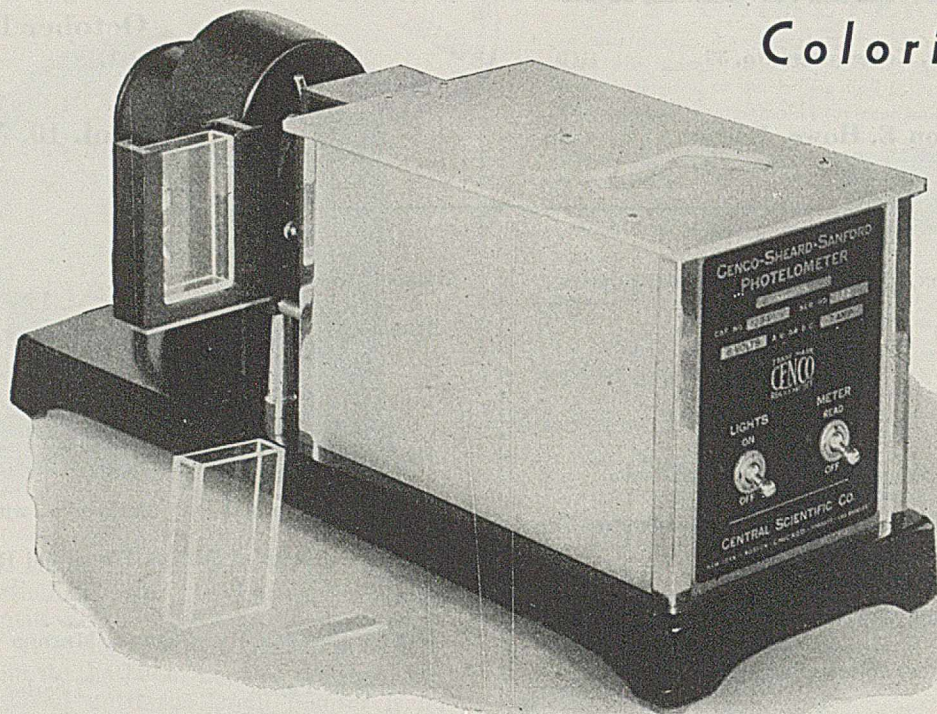
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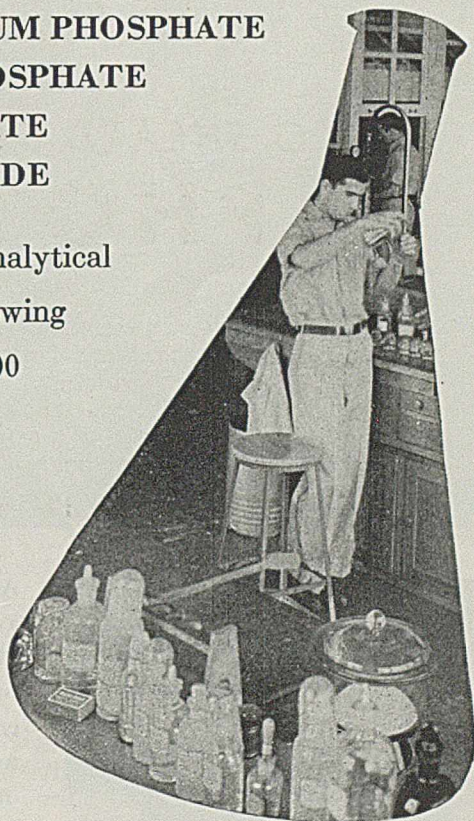
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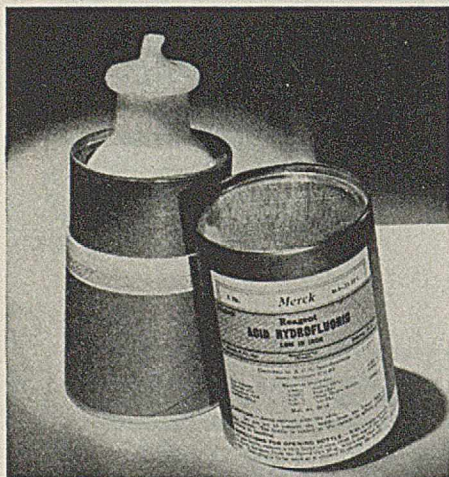
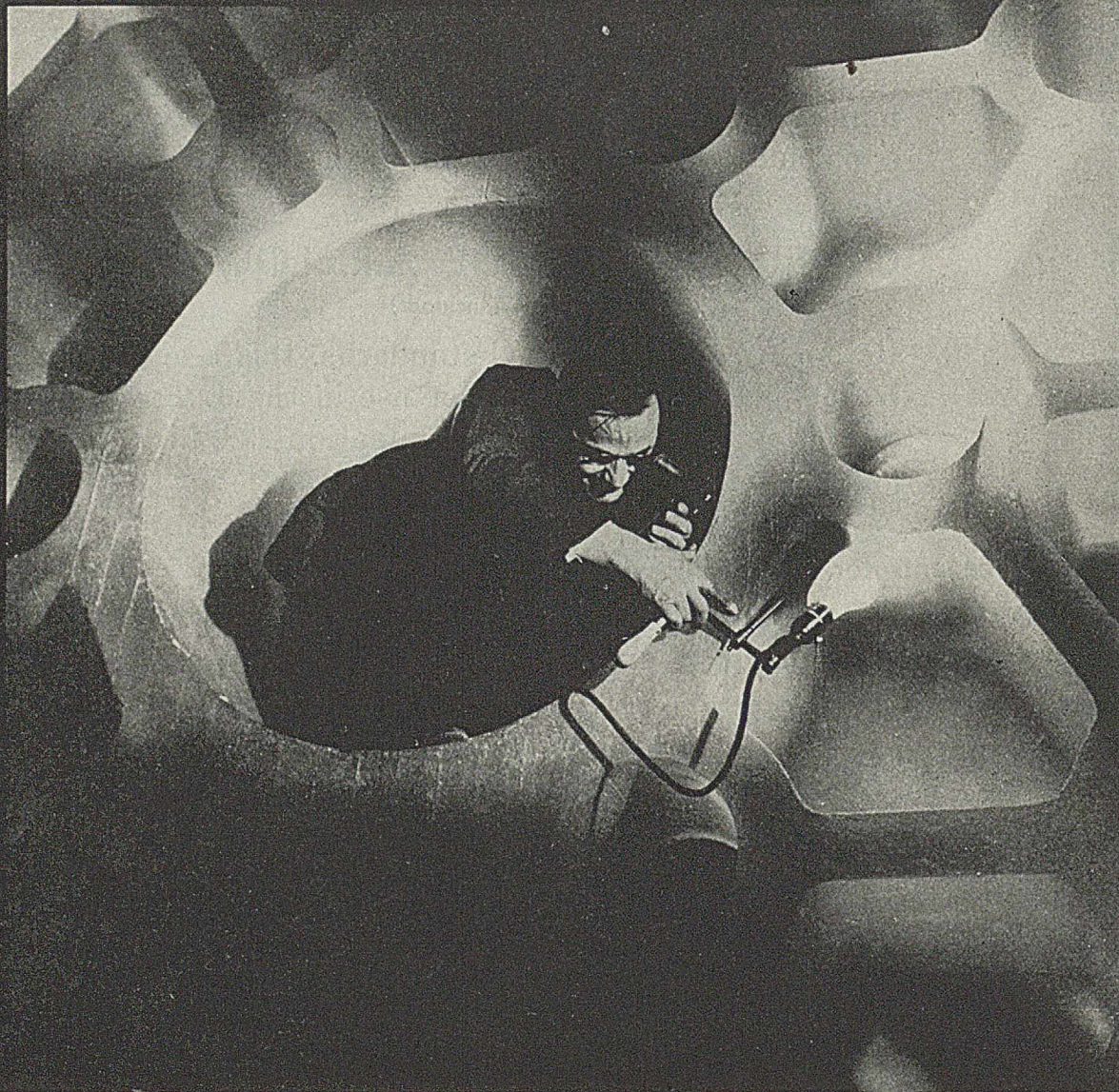
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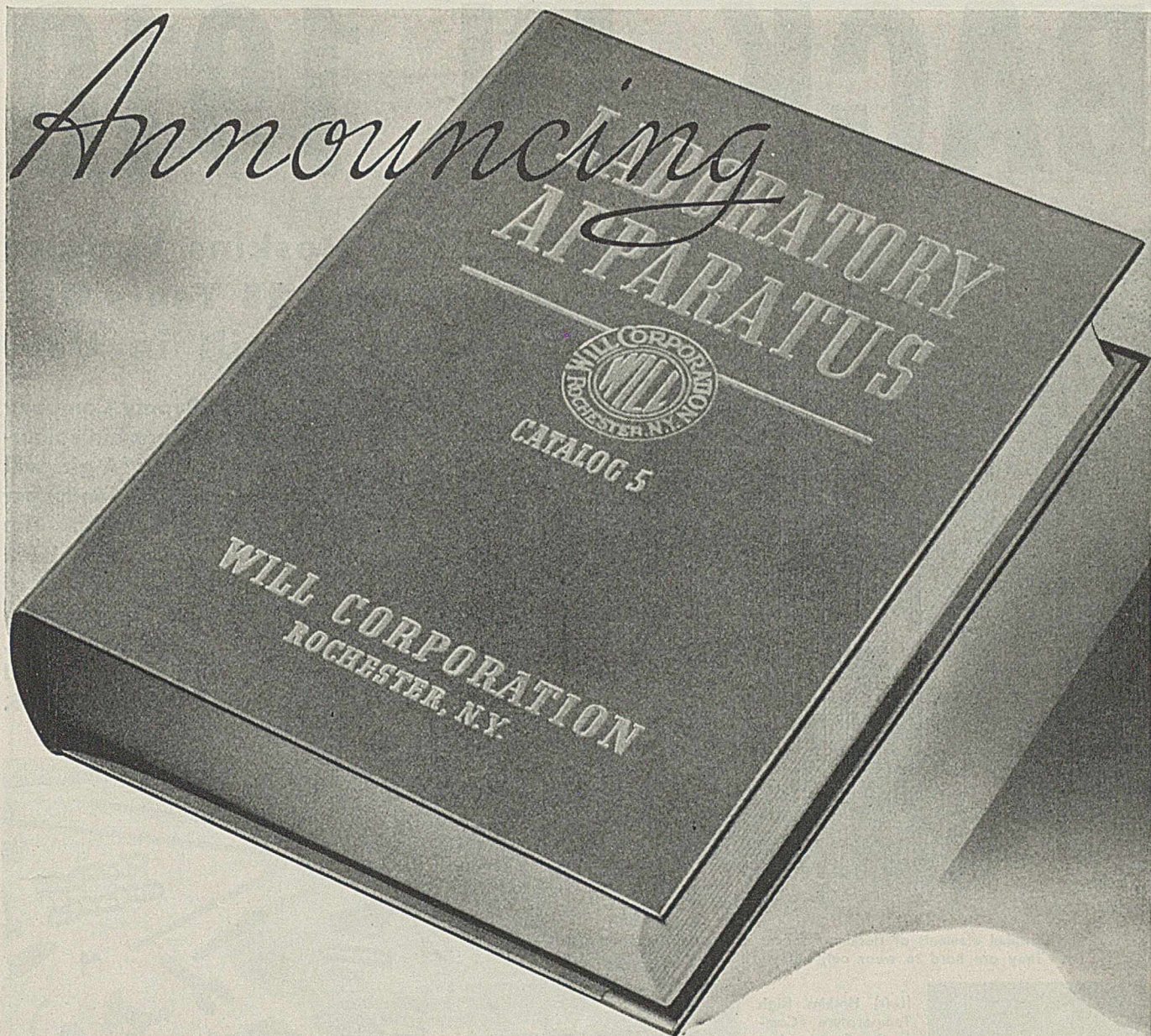
A world, yet unseen and unknown, awaits the completion of the giant 200-inch telescope, being erected on Mount Palomar, California. Scientists anxiously await the moment when the huge "eye" can be focused on distant planets to determine, among other things, what types of life, if any, exist in the far reaches of the universe.

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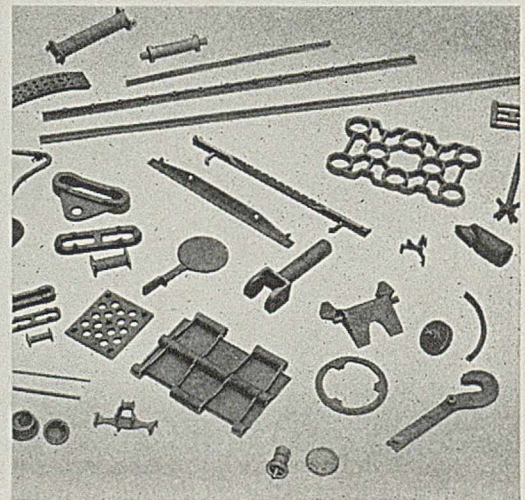
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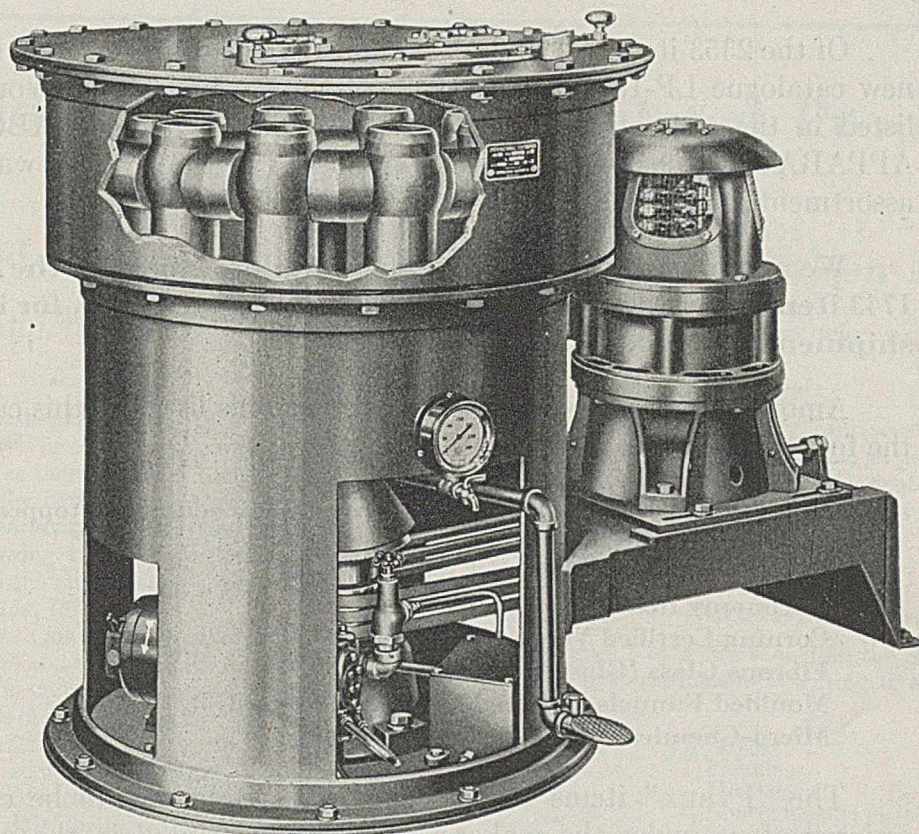
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INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

Harrison E. Howe, Editor

Refraction, Dispersion, and Related Properties of Pure Hydrocarbons Arranged for Use in the Analysis of Hydrocarbon Mixtures¹

A. L. WARD, The United Gas Improvement Co., Philadelphia, Pa., AND S. S. KURTZ, JR., The Sun Oil Company, Marcus Hook, Pa.

IN THE technical analysis of hydrocarbon mixtures and in most phases of research on pure hydrocarbons and hydrocarbon mixtures there has long been a well recognized need for concise tables listing sound values for the physical properties of hydrocarbons of the various homologous series and for graphs showing the more important relationships that may be used in the analysis and study of hydrocarbons (25, 41, 56, 87, 125, 155, 157, 158).

This paper presents a mass of data collected by the authors over a period of years and recently revised and correlated to make the information as useful as possible. The available data for the members of the common hydrocarbon series boiling between 10° and 200° C. or slightly higher have been thoroughly combed; some data for higher boiling compounds are included, but, in this article, no attempt has been made to tabulate or evaluate data for mixed type hydrocarbons such as those covered by the excellent article of Mikeska (102).

The data tabulated are (1) boiling point at 760 mm. (or 10 mm.); (2) density d_4^{20} ; refractive index n_D^{20} ; (3) dispersion $n_F - n_C$ and two derived constants; (4) the refractivity intercept, $n - d/2$ (88); and (5) the specific dispersion $(n_F - n_C)/d$ (155). These are first tabulated in detail for ten classes of hydrocarbons; tables containing averaged data for specified boiling ranges are then presented, and graphs are drawn based on these averaged properties. A few graphs are also presented showing the relationship between density and refractive index for groups of paraffin and olefin isomers.

In the tables the compounds are arranged in the order of their boiling points, and in the graphs the other properties are in general plotted against boiling point, since this arrangement is especially convenient in analytical and research work with hydrocarbon mixtures which are obtained by distillation.

A consideration of the change in density and refractive index with change in temperature is given and curves are presented showing the coefficient of cubical expansion as a function of boiling point and the change in density per degree as a function of density.

It is also shown that the introduction of the Kurtz-Ward (88) frequency coefficient into the Sellmeier-Drude equation gives

¹ No reprints of this article have been made. Those interested may purchase separate copies of this issue of the ANALYTICAL EDITION so long as the supply lasts from the Business Manager of the AMERICAN CHEMICAL SOCIETY, Mills Bldg., Washington, D. C. The price is fifty cents to non-members of the SOCIETY and forty cents to members.

an equation that accurately expresses the relationship between refractive index and density in the case of the excellent data of Gibson and Kincaid (57) for benzene over the temperature range of 25° to 45° C. and the pressure range of 1 to 1200 bars.

Tabulated Data for the Physical Properties of Pure Hydrocarbons

In Tables I to X are tabulated the properties of some individual hydrocarbons representing 10 series arranged in the following order:

- Noncyclic
 - Paraffins
 - Monoolefins
 - Nonconjugated diolefins
 - Conjugated diolefins
- Monocyclic
 - Naphthenes (saturated)
 - Monoolefins
 - Conjugated diolefins
 - Aromatics
- Polycyclic
 - Dicyclic saturated
 - Tricyclic saturated

The data have been selected from the large mass of data in the literature as being the best now available, consideration being given to the reliability of the author and to the relationship between the different physical properties as a function of the constitution of the hydrocarbon.

In a limited number of cases in which there is little to choose between sets of data, two or more sets have been averaged. In a few cases in which no sound data are available, questionable values have been included and indicated. Except in rare instances, this has been done only in the case of hydrocarbons of types for which few data are available. In most instances, references to the original literature are given; otherwise reference is made to one of the recent tabulations.

In preparing these tables it was decided to tabulate boiling points to the nearest °C. only and to correct to 760 mm. using the chart of Wilson (169), unless the pressures were very low, in which case they were corrected to 10 mm., using the chart of Nelson (108). Pressures differing by only a few millimeters from 760 were corrected with a special large-scale chart derived from Wilson's equation.

TABLE I. PHYSICAL PROPERTIES OF PARAFFINS

	Approximate Boiling Point °C.	d_4^{20}	n_D^{20}	Refractivity Intercept at 20°	Dispersion $\times 10^4 \frac{F-C}{F-C}$	References
Pentane	9	0.6130	1.35193	1.0441	62	161
2,2-Dimethylpropane	28	0.6197	1.3539	1.0441	100	159
Iso (2-methylbutane)	36	0.6262	1.3574	1.0443	63	100, 9, 71
Normal						
Hexanes						
2,2-Dimethylbutane	50	0.6493	1.3690	1.0444	64	99, 48, 159
2,3-Dimethylbutane	58	0.6615	1.3750	1.0444	65	97, 51
Iso (2-methylpentane)	60	0.6532	1.3715	1.0449	64	99, 159
3-Methylpentane	63	0.6640	1.3764	1.0444	65	98
Normal	69	0.6595	1.3750	1.0452	67	101, 89, 154, 159
Heptanes						
2,2-Dimethylpentane	79	0.6737	1.3823	1.0455	67	99, 42
2,4-Dimethylpentane	81	0.6745	1.3823	1.0451	66	98, 42
3,3-Trimethylpentane	81	0.6800	1.3864	1.0444	68	98, 42
2,3-Dimethylpentane	86	0.6852	1.3891	1.0445	67	97, 42, 150, 154
2,3-Dimethylpentane	90	0.6951	1.3920	1.0445	67	96, 72
Iso (2-methylhexane)	90	0.6787	1.3850	1.0457	67	99, 72
3-Methylhexane	92	0.6870	1.3887	1.0452	67	98, 42
3-Ethylhexane	93	0.6984	1.3937	1.0445	67	96, 42
Normal	98	0.6839	1.3878	1.0459	67	98, 39, 42, 70, 159, 140
Octanes						
2,2,4-Trimethylpentane (iso-octane)	99	0.6918	1.3916	1.0457	69	100, 163
2,2,3,3-Tetramethylbutane	107	Solid, m. p. 106.5				60
2,2-Dimethylhexane	107	0.6953	1.3930	1.0454	70	100, 96
2,4-Dimethylhexane	109	0.6993	1.3952	1.0456	69	100, 159
2,5-Dimethylhexane	109	0.6943	1.3928	1.0456	69	100, 159
2,3-Trimethylhexane	110	0.7173	1.4030	1.0444		163
3,3-Trimethylhexane	112	0.7096	1.4006	1.0458		25
2,3,4-Trimethylpentane	113	0.7197	1.4045	1.0447		163
2,3,3-Trimethylpentane	114	0.7258	1.4074	1.0445		163
2-Methyl-3-ethylpentane	115	0.7123	1.4013	1.0451	71	100, 159
2,3-Dimethylhexane	115	0.7090	1.3992	1.0446	70	99, 25
4-Methylheptane	117	0.7080	1.3936	1.0446	70	99, 25
Iso (2-methylheptane)	118	0.6980	1.3936	1.0446	70	99, 25
3,4-Dimethylhexane	118	0.7195	1.4043	1.0456	72	101, 159
3-Methyl-3-ethylpentane	118	0.7274	1.4078	1.0441		159
3-Ethylhexane	119	0.7130	1.4017	1.0452	70	99, 47
3-Methylheptane	119	0.7051	1.3980	1.0454	70	99, 35
Normal	125	0.7028	1.3976	1.0462	70	100, 39, 154, 159
Nonanes						
2,2,5-Trimethylhexane	126	0.7081	1.3987	1.0447		76
2,2,5-Trimethylhexane	130	0.7158	1.4051	1.0472		60
2,6-Dimethylheptane	132	0.7129	1.4028	1.0464		76
2,4-Dimethylheptane	136	0.7162 ^a	1.4036 ^a	1.0455		35
2,5-Dimethylheptane	138	0.7145 ^a	1.4042	1.0470		35
3,3-Dimethylhexane	138	0.7304	1.4095	1.0443		110
3,3-Diethylpentane	139	0.7522	1.4197	1.0436		105
4-Ethylheptane	139	0.7407	1.4156	1.0453	71	96, 111
2,3-Dimethylheptane	141	0.7235	1.4085	1.0467	72	100, 169
4-Methylheptane	142	0.7245	1.4078	1.0456	72	100, 169
2-Methylheptane	143	0.7134	1.4032	1.0465		159
3-Methylheptane	144	0.7210	1.4065	1.0460		39
Normal	150	0.7180	1.4056	1.0468		154
Decanes						
2,6-Trimethylheptane	144	0.7198	1.4057	1.0458		60
2,6-Trimethylheptane	152	0.7215	1.4090	1.0483		76
2,4,4-Trimethylheptane	153	0.7344	1.4090	1.0468		60
2,5,3-Trimethylheptane	157	0.7547	1.4224	1.0451		40
2,3,3-Tetramethylhexane	159	0.7559	1.4230	1.0454		40
3,3,3-Trimethylheptane	160	0.7900 ^a	1.4110 ^a	1.0454		71
2,6-Dimethylheptane	160	0.7344 ^a	1.4090 ^a	1.0468	72	97, 165
2,7-Dimethylheptane	160	0.7366	1.4145	1.0463		60
3,6-Dimethylheptane	160	0.7360	1.4141	1.0461		59
4-Methylheptane	162	0.7523	1.4223	1.0461		72
Iso (2-methylnonane)	166	0.7542	1.4089	1.0468	72	99, 160
5-Methylnonane	167	0.7520	1.4122	1.0459		38
3-Methylnonane	168	0.7335	1.4125	1.0458	72	100, 38
Normal	174	0.7304	1.4119	1.0466	73	100, 38, 154
Undecanes						
2,4,7-Trimethylheptane	168	0.7331	1.4132	1.0457		60
2,3,7-Trimethylheptane	175	0.7566	1.4230	1.0447		93
2,3,7-Trimethylheptane	175					

TABLE II. PHYSICAL PROPERTIES OF OLEFINS^a

	Approximate Boiling Point °C.	d_4^{20}	n_D^{20}	Refractivity Intercept at 20°	Dispersion $\times 10^4 \frac{F-C}{F-C}$	References
Pentenes						
2-Methylbutene (3)	20	0.6284	1.3653	1.0511	...	156
2-Pentene (1)	30	0.6410	1.3710	1.0505	...	156
2-Methylbutene (1)	31	0.6504	1.3777	1.0525	...	156
Pentene (2), cis	36	0.6540	1.3817	1.0547	88	134, 155
Pentene (2), trans	36	0.6486	1.3700	1.0547	...	93
2-Methylbutene (2)	38	0.6620	1.3878	1.0568	89	135, 156
Hexenes						
2,2-Dimethylbutene (3)	41	0.6510	1.3759	1.0504	...	150
2-Methylpentene (4)	54	0.6646	1.3825	1.0502	83	124, 129
3-Methylpentene (1)	54	0.6700	1.3835	1.0485	...	129
2-Methylpentene (3) (low boiling)	55	0.6702	1.3881	1.0531	...	129
2,3-Dimethylbutene (1)	56	0.6807	1.3897	1.0493	...	129
2,3-Dimethylbutene (3) (high boiling)	58	0.6709	1.3885	1.0530	...	129
2-Methylpentene (1)	62	0.6817	1.3921	1.0512	...	129
Hexene (1)	64	0.6732	1.3858	1.0492	...	129
3-Methylpentene (2) (low boiling)	66	0.6940	1.3994	1.0524	90	130, 129
2-Ethylbutene (1)	66	0.6914	1.3990	1.0533	...	129
Hexene (3)	67	0.6816	1.3942	1.0534	...	129
2-Methylpentene (2)	67	0.6904	1.4005	1.0553	90	130, 129
Hexene (2)	68	0.6813	1.3928	1.0521	91	132, 129
3-Methylpentene (2) (high boiling)	68	0.6813	1.3928	1.0521	91	132, 129
2,3-Dimethylbutene (2)	74	0.6956	1.4002	1.0524	90	130, 129
2,3-Dimethylbutene (1)	74	0.7081	1.4115	1.0575	...	129
Heptenes						
2,2-Dimethylpentene (4)	72	0.6827	1.3911	1.0498	...	162
2,2-Dimethylpentene (3)	76	0.6881	1.3986	1.0546	...	150
3-Ethylpentene (1)	77	0.6966	1.3971	1.0488	...	142
3,3-Dimethylpentene (1)	81	0.6961	1.3991	1.0511	...	150
2,4-Dimethylpentene (1)	81	0.6937	1.3970	1.0507	...	142
2,4-Dimethylpentene (2)	83	0.6947	1.4020	1.0547	87	125, 58
3-Methylhexene (1)	84	0.6949	1.3970	1.0496	...	142
2,3-Dimethylpentene (1)	84	0.7054	1.4022	1.0495	...	142
2-Methylhexene (5)	85	0.6986	1.3954	1.0486	...	142
2-Methylhexene (4) (low boiling)	86	0.7020	1.3995	1.0485	...	142
3-Methylhexene (4) (low boiling)	86	0.6981	1.4000	1.0510	...	142
2,3-Dimethylpentene (3)	86	0.7126	1.4052	1.0489	...	142
2-Methylhexene (3)	87	0.6943	1.3991	1.0520	...	142
3-Methylhexene (5)	87	0.6969	1.3985	1.0501	...	142
3-Methylhexene (4) (high boiling)	88	0.7007	1.3980	1.0477	...	142
3-Methyl-2-ethylbutene (1)	89	0.7186	1.4120	1.0527	...	142
2-Methylhexene (1)	91	0.7000	1.4000	1.0500	...	142
2-Methylhexene (4) (high boiling)	91	0.6990	1.3990	1.0495	...	142
3-Methylhexene (2)	93	0.7120	1.4080	1.0518	...	142
2-Methylhexene (2)	94	0.7079	1.4075	1.0531	...	142
2-Ethylpentene (1)	94	0.7079	1.4050	1.0511	...	142
3-Ethylpentene (2)	95	0.7172	1.4120	1.0539	...	142
Heptene (1)	95	0.6993	1.3999	1.0502	86	126, 129
Heptene (3)	96	0.7016	1.4042	1.0534	...	99
Heptene (2)	98	0.7034	1.4041	1.0524	...	129
Octenes						
2,2-Dimethylhexene (3)	100	0.7048	1.4068	1.0544	...	150
2,4,4-Trimethylpentene (1)	101	0.7151	1.4082	1.0507	...	149
(Isobutyl)ene ²	102	0.7195	1.4121	1.0515	...	91
2,4,4-Trimethylpentene (2)	105	0.7211	1.4158	1.0543	...	150
3,3-Dimethylhexene (4)	108	0.7202	1.4120	1.0519	...	150
2,3,3-Trimethylpentene (1)	112	0.7363	1.4232	1.0497	...	150
2,2,3-Trimethylpentene (3)	112	0.7395	1.4232	1.0535	...	150
3-Ethylheptene (3)	119	0.7318	1.4204	1.0545	90	123, 47
4-Methylheptene (3)	119	0.7237 ^b	1.4170 ^b	1.0552	90	125, 47
2-Propylpentene (1)	119	0.7254	1.4182	1.0552	90	122, 47
2-Methylheptene (1)	122	0.7254	1.4169	1.0542	...	47
Octene (1) ¹	124	0.7155	1.4088	1.0516	85	119, 55

2,6-Dimethylnonane	175	0.7439	1.4176	1.0456	74	100	98	32 at 10	0.7248	1.4137	1.0513	...	96
Normal	195	0.7404	1.4173	1.0471	mm.
5-Ethylnonane	60 at 10 mm.	0.7507	1.4205	1.0452	66	...	0.7197 ^b	1.4136 ^b	1.0538	87	121
Dodecanes													
2,6-Dimethyl-3-isopropylheptane	187	0.7655	1.432	1.0483	60	134	0.761	1.4305	1.0500	...	163
2-Methyl-5-propyloctane	189	0.7496	1.422	1.0472	60	137	0.742	1.4233	1.0523	...	160
2,6-Dimethyldecane	195	0.7572	1.4240	1.0484	60	139	0.743	1.4233	1.0523	...	41
3-Propylnonane	205	0.7559	1.4228	1.0448	69	140	0.747	1.4250	1.0515	...	160
Normal	216	0.7495	1.4217	1.0470	76	101	39, 180	142	0.744 ^b	1.4249	1.0542	90	121
2,3,6,7-Tetramethyloctane	75 at 10 mm.	0.7630	1.4275	1.0460	60	145	0.7409	1.4247	1.0542	...	164
3-Methylhendecane	84 at 10 mm.	0.7527	1.4238	1.0465	60	147	0.7552	1.4236	1.0510	...	117
Tridecanes													
2,5,9-Trimethyldecane	208	0.7692	1.4297	1.0451	60	150	0.749	1.4236	1.0510	...	41
4-Propyldodecane	222	0.7609	1.4272 ^a	1.0468	75	98	47	59 at 10 mm.	0.7302	1.4160	1.0509	...	99
5-Methyltridecane	227	0.7576	1.4244	1.0456	60	158	0.745	1.4271	1.0546	...	41
Normal	234	0.7571	1.4244	1.0456	84	160	0.7418	1.4255	1.0546	...	135
5-n-Butylnonane	...	0.7615 ^a	1.4273 ^a	1.0466	74	97	47	161	0.7502 ^b	1.4291 ^b	1.0540	88	119
Tetradecanes													
4,5-Di-n-propyloctane	220	0.7770	1.4334	1.0472	116	162	0.749	1.4273	1.0538	...	135
Normal	253	0.7645	1.4332	1.044	84	163	0.7530	1.4301	1.0536	90	118
Pentadecanes													
4-Methyl-6-propylhendecane	237	0.7723	1.4325	1.0464	60	164	0.7580	1.4303	1.0554	...	171
6-Methyl-7-ethyltridecane	243	0.7782	1.4355	1.0464	60	164	0.7545	1.4308	1.0554	...	164
Unknown	244	0.7727	1.4329	1.0465	60	164	0.7545	1.4308	1.0554	...	164
6-Propyldodecane	244	0.7720	1.4326	1.0466	41	167	0.7568	1.4333	1.0544	...	41
2,6,10-Trimethyltridecane	248	0.7717	1.4324	1.0466	60	167	0.7578	1.4333	1.0544	...	164
Unknown	264	0.779	1.4332	1.044	166	179	0.7600	1.4306	1.0506	...	91
Normal	271	0.7689	1.433	1.049	60	188	0.7774	1.444	1.055	...	106
Hexadecanes													
7,8-Dimethyltridecane	264	0.785	1.4352	1.0482	60	192	0.7609	1.434	1.0535	...	28
Normal	288	0.7741	1.4352	1.0482	24	211	0.7590	1.4270	1.0475	...	41
4,7-Di-n-propyldodecane	128 at 10 mm.	0.7841	1.4368	1.0448	60	214	0.758	1.4270	1.0475	...	41
6,9-Dimethyltridecane	136 at 10 mm.	0.7787	1.4348	1.0454	60	214	0.758	1.4270	1.0475	...	41
3-Ethyltridecane	148 at 10 mm.	0.7789	1.4366	1.0472	77	99	47	77 at 10 mm.	0.7612	1.4401	1.0551	...	164
Heptadecanes													
Normal	303	0.7778	1.4374	1.0485	76	98	47	80 at 10 mm.	0.7643	1.4362	1.0541	...	164
Unknown	153 at 10 mm.	0.780	1.4376	1.0476	166	83 at 10 mm.	0.7647	1.4368	1.0543	...	164
Octadecanes													
Normal	316	0.7818 ^b	1.4395 ^a	1.0486	75	96	47	85 at 10 mm.	0.7715	1.4391	1.0534	89	116
3,12-Dimethyltridecane	156 at 10 mm.	0.7924	1.4428	1.0466	60	97 at 10 mm.	0.7701	1.4401	1.0551	...	164
2-Methylheptadecane	178 at 10 mm.	0.7806 ^c	1.4385 ^a	1.0486	77	99	47	246	0.775	1.4446	1.0525	94	120
Nonadecanes													
Normal	330	0.7854 ^b	1.4404 ^b	1.0477	75	96	60	116 at 10 mm.	0.7843	1.4446	1.0525	94	120
Eicosanes													
3-Ethyltridecane	182 at 10 mm.	0.7928 ^a	1.4441 ^a	1.0477	78	98	47	137 at 10 mm.	0.7737	1.4365	1.0501	...	96
Normal	193 at 10 mm.	0.7888 ^b	1.4434 ^b	1.0490	60	274	0.7811	1.4419	1.0514	84	108
2-Methylnonadecane	196 at 10 mm.	0.7864 ^a	1.4413 ^a	1.0481	78	99	47	113 at 10 mm.	0.7944	1.4482	1.0510	...	91
Heptacosane	...	0.7766	1.4356	1.0479	76	98	60	144 at 10 mm.	0.7917 ^b	1.4472 ^b	1.0514	88	110
Docosane	...	0.7968	1.4463	1.0479	60	157 at 10 mm.	0.7830	1.4417	1.0502	...	96
4-n-Propylnonadecane	211 at 10 mm.	0.7979	1.4461	1.0476	75	99	60	...	0.8021 ^b	1.4466 ^b	1.0456	86	107
Tricosanes													
Tetracosane	...	0.8054	1.4502	1.0475	60	161 at 10 mm.	0.778	1.4466	1.0456	86	107
4,8,13,17-Tetramethyltricosane	...	0.8105	1.4533	1.0481	60
2,6,10,14,18,22-Hexamethyltricosane	...	0.8230	1.4594	1.0479	141
Tricosane	...	0.8327	1.4606	1.0443	141
16-Ethyltridecane	...	0.8558	1.4753	1.0474	75	96	143
Pentatriacontane
16-Butyltridecane
Hydrogenated rubber (C ₂₄ H ₄₀) ₂

^a Nomenclature. The side chain rather than the double bond is given the smallest possible number. Thus $\text{C}-\text{C}=\text{C}$ is called 2-methylpentene (4) rather than 4-methylpentene (1).

^b Calculated from some other temperature than 20° C.

^c Calculated to hypothetical liquid state at 20° C.

TABLE II. PHYSICAL PROPERTIES OF OLEFINS (Concluded)

	Approximate Boiling Point ° C.	d_4^{20}	n_D^{20}	Refractivity Intercept at 20°	Dispersion $\times 10^4 \frac{F-C}{d}$	References
Octadecenes						
Octadecene (1)	170 at 10	0.7898	1.4451	1.0502	...	41
2-Methylheptadecene (2)	176 at 10	0.7908 ^b	1.4507	1.0553	88	111
Eicosenes (Isobutylene)5	184 at 10	0.8176	1.4601	1.0513	...	91
3-Methylnonadecene (2)	190 at 10	0.8000 ^b	1.4518 ^b	1.0518	88	110
2-Methylnonadecene (2)	200 at 10	0.7994 ^b	1.4522 ^b	1.0525	89	109
Henicosene	199 at 10	0.801	41
Henicosene (9)	191 at 10	0.8340	1.4684	1.0514	...	91
Tetracosene (Isobutylene)6	219 at 10	0.8455	1.4739	1.0512	...	91
Octacosene (Isobutylene)7	...	0.9237	1.5219	1.0601	...	38

^b Calculated from some other temperature than 20° C.

TABLE III. PHYSICAL PROPERTIES OF DIOLEFINS

	Approximate Boiling Point ° C.	d_4^{20}	n_D^{20}	Refractivity Intercept at 20°	Dispersion $\times 10^4 \frac{F-C}{d}$	References
Pentadiene (1,4)	26	0.6594	1.3880	1.0583	...	83
Pentadiene (2,3)	50	0.7023	1.3919	1.0651	...	86
Pentadiene (1,5)	60	0.6536
Hexadiene (1,5)	60	0.6903	1.4028	1.0577	100	145
Hexadiene (1,4)	64	0.6996	1.4162	1.0664	...	137
2-Methylpentadiene (2,3)	72	0.711	70
Heptadiene						
2,2-Dimethylpentadiene (3,4)	82	0.7183	1.4258 ^a	1.0675	...	49
2,4-Dimethylpentadiene (2,3)	86	0.7167 ^a	1.4202	1.0614	...	101
Heptadiene (1,4)	92	0.7176	1.4292 ^a	1.0586	105	145
2-Methylheptadiene (1,5)	92	0.7276 ^a	1.4324 ^a	1.0689	...	25
Heptadiene (1,2)	106	0.7306	1.4322	1.0689	...	25
Octadienes						
2,5-Dimethylhexadiene (1,5)	116	0.7466	1.4395	1.0662	...	64
Octadiene (1,5)	118	0.7314	1.4265	1.0608	...	25
3-Ethylhexadiene (2,5)	123	0.7548	119
Octadiene (1,4)	127	0.754	41
Nonadienes						
2,6-Dimethylheptadiene (1,5)	141	0.7642	1.4445	1.0624	108	140
2,6-Dimethylheptadiene (2,7)	144	0.7692	1.4460	1.0614	108	140
2,6-Dimethylheptadiene (1,2)	144	0.7628	1.4408	1.0594	109	143
Decadienes						
3,6-Dimethyloctadiene (2,6)	154	0.7767	1.4445	1.0562	...	73
2,6-Dimethyloctadiene (2,7)	163	0.7629	1.4387	1.0573	103	135
2,6-Dimethyloctadiene (2,7) ^b	166	0.7882	1.453	1.061	...	151
2,7-Dimethyloctadiene (2,6)	166	0.7849	1.4481	1.0567	...	73
2,6-Dimethyloctadiene (2,6)	166	0.7859	1.4490	1.0560	...	73
2,6-Dimethyloctadiene (2,7)	166	0.7736	1.4481	1.0620	108	140
2,6-Dimethyloctadiene (2,7)	52 at 10	0.7767	1.4507	1.0624	...	153

^b Calculated from some other temperature than 20° C.

TABLE V. PHYSICAL PROPERTIES OF SATURATED CYCLICS (NAPHTHENES)

	Approximate Boiling Point ° C.	d_4^{20}	n_D^{20}	Refractivity Intercept at 20°	Dispersion $\times 10^4 \frac{F-C}{d}$	References
1,1-Dimethylcyclopropane	21	0.6604	1.3659	1.0357	172	106
1,2-Dimethylcyclopropane	33	0.6792 ^a	1.3764 ^a	1.0373	...	118, 176
Ethylcyclopropane	36	0.6832	1.3791	1.0375	...	123
Methylcyclobutane	36	0.6935	1.3837	1.0370	...	58
Cyclopentane	50	0.7454	1.4064	1.0337	74	98
1,1,2-Trimethylcyclopropane	53	0.6949	1.3870	1.0396	77	111
Ethylcyclobutane	72	0.7279	1.4020	1.0381	...	189
Methylcyclopentane	72	0.7472	1.4101	1.0365	72	96
Cyclohexane	81	0.7781	1.4270	1.0373	78	100
1-Methyl-2-isopropylcyclopropane	81	0.7101	1.3927	1.0377	...	76
1,1-Dimethylcyclopentane	87	0.7547	1.4137	1.0366	...	34, 76
1,3-Dimethylcyclopentane	91	0.7479	1.4099	1.0360	...	41
1,2-Dimethylcyclopentane (low boiling)	92	0.7495	1.4114	1.0367	73	97
1,2-Dimethylcyclopentane (high boiling)	99	0.7718	1.4223	1.0364	74	96
Methylcyclohexane	100	0.7707	1.4243	1.0390	79	102
Ethylcyclopentane	101	0.7610	1.4182	1.0377	72	95
1-Methyl-1,2-diethylcyclopropane	108	0.7381	1.4102	1.0412	...	41
1-Methyl-2-isobutylcyclopropane	110	0.7402	1.4088	1.0387	...	177
1,2,4-Trimethylcyclopentane	113	0.7565	1.4165	1.0374	74	98
1,2,3-Trimethylcyclopentane	114	0.7595	1.4194	1.0397	75	99
1,1,2-Trimethylcyclopentane	114	0.7718	1.4226	1.0370	75	97
Cycloheptane	119	0.8099	1.4440	1.0391	...	123
1,4-Dimethylcyclohexane (trans)	119	0.7655	1.4205	1.0378	75	98
1,3-Dimethylcyclohexane (trans)	119	0.762	1.4248	1.0438	77	101
1,3-Dimethylcyclohexane (cis)	121	0.7735	1.4259	1.0392	77	100
1,4-Dimethylcyclohexane (cis)	121	0.7671	1.4226	1.0391	77	100
1,3-Diethylcyclohexane	122	0.7973	1.4388	1.0402	...	175
1,1-Dimethylcyclohexane	123	0.7809 ^a	1.4305	1.0401	78	100
1,1-Dimethylcyclohexane	120	0.7800	1.4294	1.0394	...	84
1,4-Diethylcyclohexane	123	0.800	1.4415	1.0415	77	100
1,2-Dimethylcyclohexane (trans)	124	0.7760	1.4270	1.0390	76	98
1,2-Dimethylcyclohexane (cis)	127	0.7963	1.4360	1.0370	76	98
Isopropylcyclopentane	129	0.7717	1.4248	1.0394	75	97
Propylcyclopentane	130	0.7718	1.4250	1.0391	75	97
Ethylcyclohexane	130	0.7840	1.4324	1.0404	76	97
1,1,2,3-Tetramethylcyclopentane	133	0.7763 ^a	1.4271 ^a	1.0380	77	100
1,1,3-Trimethylcyclohexane (cis)	133	0.8265	1.4565	1.0433	...	132
1,1,3-Trimethylcyclohexane (cis)	138	0.7930	1.4367	1.0402	...	44
1,3-Dimethyl-2-ethylcyclohexane	138	0.7756	1.4274	1.0396	75	97
1,3,5-Trimethylcyclohexane	139	0.7720	1.4270	1.0410	77	100
1,2,4-Trimethylcyclohexane	140	0.7813	1.4311	1.0405	77	99
1,2,5-Trimethylcyclohexane	140	0.7742	1.4290	1.0419	78	101
1,3,5-Trimethylcyclohexane (cis)	140	0.7769	1.4299	1.0415	77	100
1-Methyl-5-isopropylcyclopentane	142	0.7754 ^a	1.4271 ^a	1.0394	76	98
1,2,4-Trimethylcyclohexane (cis)	142	0.7850	1.4333	1.0408	78	99
1-Methyl-2-isopropylcyclopentane	143	0.7792	1.4279	1.0383	77	99
1,2,3-Trimethylcyclohexane (trans)	143	0.7914	1.4357	1.0400	78	99
1,1,2-Trimethyl-3-isopropylcyclobutane	146	0.7930	1.4367	1.0402	79	99
1,1,2-Trimethyl-3-isopropylcyclobutane	146	0.7598	1.4200	1.0401	75	99
Isobutylcyclopentane	149	0.7795	1.4294	1.0397	78	100
1,3-Methylcyclohexane	149	0.814	1.4487	1.0417	...	168
Cyclooctane	150	0.839	1.4586	1.0391	...	138
1-Methyl-2,3-diisopropylcyclopentane	151	0.779	1.4305	1.0410	...	59
1,4-Diethylcyclohexane	151	0.789	1.4343	1.0398	...	138
1,1-Diethylcyclopentane	151	0.8027	1.4388	1.0375	...	76
1,2-Methylcyclohexane	153	0.803	1.4400	1.0385	...	138
Isopropylcyclohexane	153	0.7902	1.4363	1.0412	77	99
n-Propylcyclohexane	156	0.7898	1.4358	1.0409	78	99
1,2-Dimethyl-3,4-diethylcyclobutane	156	0.7729	1.4248	1.0384	76	98

Compound	158	0.7755	1.4279	1.0402	90
1,2-Diisopropylcyclobutane	158	0.7755	1.4279	1.0402	90
1,2-Dimethyl-3-isopropylcyclopentane	160	0.7885	1.4329	1.0387	41
1,2,3,5-Tetramethylcyclohexane (trans)	163	0.8140	1.4465	1.0395	77
1-Methyl-2,5-diethylcyclopentane	164	0.7839	1.4308	1.0398	76
1,2,4,5-Tetramethylcyclohexane (trans)	167	0.8100	1.4444	1.0394	77
1-Methyl-4-isopropylcyclohexane	168	0.7962	1.4375	1.0394	78
1,2,3,5-Tetramethylcyclohexane (cis)	169	0.8166	1.4484	1.0401	85
Isobutylcyclohexane	170	0.7950	1.4389	1.0414	98
1-Methyl-2-isopropylcyclohexane	170	0.811	1.4464	1.0409	138
1,2,4,3-Tetramethylcyclohexane (G)	171	0.8142	1.447	1.040	...
1,3-Methyl-n-propylcyclohexane	171	0.8122	1.4462	1.0401	83
1,2-Methyl-n-propylcyclohexane	172	0.794	1.4377	1.0407	102
1,6-Methyl-n-propylcyclohexane	176	0.808	1.4445	1.0405	138
1,5-Methyl-n-propylcyclohexane	176	0.796	1.4393	1.0413	138
1,2,3-Trimethylcyclohexane	178	0.7944	1.4361	1.0389	77
1,2,3-Triethylcyclopentane	178	0.7955	1.4365	1.0387	77
sec-Butylcyclohexane	179	0.809	1.4458	1.0413	138
n-Butylcyclohexane	180	0.797	1.4408	1.0423	138
Isomylcyclohexane	194	0.798	1.4420	1.0430	138
tert-Amylcyclohexane	194	0.8196	1.4520	1.0422	138
1,3-Methyl-n-butylcyclohexane	195	0.801	1.4418	1.0413	138
1,4-Methyl-n-butylcyclohexane	196	0.805	1.4415	1.0390	138
1,2-Methyl-n-butylcyclohexane	197	0.811	1.4467	1.0412	138
n-Amylcyclohexane	202	0.802	1.4428	1.0418	138
2,18	218	0.814	1.4487	1.0417	138
1,2-Methyl-n-amylycyclohexane	112 at 10	0.8142	1.4475	1.0404	174

^a Value calculated from some temperature other than 20° C.

Compound	182	0.7934	1.4537	1.0570	46
Undecadienes	182	0.7934	1.4537	1.0570	46
2,6-Dimethylnonadiene (2,6)	182	0.8033	1.4571	1.0555	46
2,6,7-Trimethyloctadiene (2,6)	188	0.769	1.4398	1.0553	27
Undecadiene (1,10) ^b	201	0.7970	1.4555	1.0570	46
Dodecadienes	214	0.7973	1.4558	1.0571	46
2,6-Dimethyldecadiene (2,6)	84 at 10	0.7813	1.4490	1.0554	137
2,6,9-Trimethyldecadiene (2,6)	99	0.7873	1.4490	1.0554	126
2,6-Dimethyldecadiene (x,x)	126	0.7873	1.4490	1.0554	126
Tridecadienes	187	0.7873	1.4490	1.0554	126
2,6-Dimethylundecadiene (x,x)	187	0.7873	1.4490	1.0554	126

^a Value calculated from some temperature other than 20° C.

^b Best data available, but questionable.

TABLE IV. CONJUGATED DIOLEFINS

Compound	Approximate Boiling Point °C.	d ₄ ²⁰	n _D ²⁰	Refractivity at 20°	Dispersion × 10 ⁴ F-C	References
Pentadienes						
2-Methylbutadiene (1,3)	34	0.6805	1.4216	1.0814	155	225
(isoprene)	43	0.6815 ^a	1.4309 ^a	1.0902	166	243
Pentadiene (1,3) (piperylene)	70	0.7261	1.4394	1.0763	145	200
Hexadienes						
2,3-Dimethylbutadiene (1,3) ^b	73	0.7152	1.4418	1.0840	163	226
Hexadiene (1,3)	76	0.7193	1.4520	1.0934	162	226
2-Methylpentadiene (2,4)	76	0.7196	1.4467	1.0869	158	222
2-Methylpentadiene (1,3)	76	0.7108	1.4427	1.0873	168	222
Hexadiene (2,4) (low boiling)	78	0.7279	1.4511	1.0877	164	225
3-Methylpentadiene (1,3)	79	0.7152	1.4493	1.0907	166	232
Hexadiene (2,4) (high boiling)	80	0.7205	1.4514	1.0912
Hexadiene (2,5)	93	0.7432	1.4428	1.0712	155	208
Heptadienes						
2,3-Dimethylpentadiene (1,3) ^b	93	0.7368	1.4405	1.0721
2,4-Dimethylpentadiene (1,3) ^b	102	0.7448 ^a	1.4550 ^a	1.0826	168	226
3-Methylhexadiene (1,3)	104	0.7439	1.4611	1.0893	159	214
2-Methylhexadiene (2,4)	105	0.7340	1.4494	1.0814	159	214
Heptadiene (2,4)	108	0.7585	1.4591	1.0799
3-Methylhexadiene (2,4)	115	0.7607	1.4530	1.0727	151	206
Octadienes						
2,4-Dimethylhexadiene (2,4) ^b	117	0.7323	1.4505	1.0844	151	206
2,3-Dimethylhexadiene (3,5)	117	0.7412	1.4502	1.0796	151	200
2,5-Dimethylheptadiene (1,3) ^b	132	0.7590	1.4645	1.0850
4-Methylheptadiene (2,4)	133	0.7825	1.4852	1.0740
3,4-Dimethylhexadiene (2,4) ^b	134	0.7625	1.4623	1.0811
3-Methylheptadiene (2,4)	141	0.7481	1.4571	1.0783
Nonadienes						
2,6-Dimethylheptadiene (2,4)	141	0.7567	1.4571	1.0783
2,6-Dimethylheptadiene (1,3) ^b	145	0.7692	1.4604	1.0758	148	197
3,5-Dimethylheptadiene (2,4) ^b	149	0.7591	1.4553	1.0803	157	204
7-Methyloctadiene (2,4)	149	0.7595	1.4553	1.0780
2-Methyloctadiene (4,6) ^b	150	0.7679	1.4652	1.0812
4-Methylheptadiene (3,5)	165	0.7792	1.4637	1.0741
Decadienes						
2,6-Dimethyloctadiene (3,5) ^b	166	0.7790	1.4640	1.0745
2,6-Dimethyloctadiene (4,6) ^b	52 at 10	0.7767	1.4607	1.0724
2,6-Dimethyloctadiene (x,x)	165	0.7817	1.4632	1.0724
Undecadienes						
2,6-Dimethylnonadiene (4,6) ^b	165	0.7817	1.4632	1.0724

^a Value calculated from some temperature other than 20° C.

^b Best data available, but questionable.

TABLE VI. UNSATURATED CYCLICS

Compound	Approximate Boiling Point °C.	d ₄ ²⁰	n _D ²⁰	Refractivity at 20°	Dispersion × 10 ⁴ F-C	References
1-Methylcyclobutene (1)	38	0.7105 ^a	1.4052 ^a	1.0500	...	53
Cyclopentene	44	0.7742 ^a	1.4230 ^a	1.0359	...	73
1-Methylcyclopentene (3)	73	0.772	41
1-Methylcyclopentene (1)	73	0.7757	98
1,1-Dimethylcyclopentene (2)	79	0.7579	1.4190	1.0405	...	74
Cyclohexene	83	0.8101	1.4465	1.0415	97	119
1,2-Dimethylcyclopentene (1)	97	0.7831	1.4348	1.0433	...	84
1,2-Dimethylcyclopentene (2)	103	0.784	1.442	1.047	...	84
1-Methylcyclohexene (3)	103	0.7985	41
1-Methylcyclohexene (2)	105	0.805	41
1,2-Dimethylcyclohexene (5)	105	0.7952	1.4442	1.0466	...	34
1-Ethylcyclohexene (2)	108	0.796	1.443	1.045	...	41
1-Ethylcyclopentene (1)	109	0.7974	1.4426	1.0439	...	41
1,1,2-Trimethylcyclopentene (2)	109	0.7827 ^a	1.4331 ^a	1.0417	...	41, 154
1-Methylcyclohexene (1)	111	0.8103 ^a	1.4497	1.0446	...	47
Cycloheptene	114	0.8228	1.4552	1.0438	...	10
1,1-Dimethylcyclohexene (3)	120	0.8028 ^a	1.4442 ^a	1.0428	93	116
4,4-Dimethylcyclohexene (1)	121	0.8024	1.443	1.042	...	14 av.
1,2,3-Trimethylcyclopentene (1)	121	0.7970 ^a	1.4445 ^a	1.0460	...	41
3,4-Dimethylcyclohexene (1)	124	0.807	1.444	1.041	...	47
3,5-Dimethylcyclohexene (1)	124	0.801	1.444	1.044	...	41
1,2-Dimethylcyclohexene (3 and 4)	125	0.8064	1.4454	1.0422	92	114

^a Calculated from some other temperature than 20° C.

(Continued on page 564)

TABLE VI. UNSATURATED CYCLICS (Concluded)

Approximate Boiling Point °C.	d ₄ ^{20°}	n _D ^{20°}	Refractive Index at 20°	Dispersion × 10 ⁴ F-C	References																																																																																																																																																																																																																																			
						1,3-Dimethylcyclohexene (3)	1,3-Dimethylcyclohexene (4)	1,3-Dimethylcyclohexene (5)	1,3-Dimethylcyclohexene (6)	1,3-Dimethylcyclohexene (7)	1,3-Dimethylcyclohexene (8)	1,3-Dimethylcyclohexene (9)	1,3-Dimethylcyclohexene (10)	1,3-Dimethylcyclohexene (11)	1,3-Dimethylcyclohexene (12)	1,3-Dimethylcyclohexene (13)	1,3-Dimethylcyclohexene (14)	1,3-Dimethylcyclohexene (15)	1,3-Dimethylcyclohexene (16)	1,3-Dimethylcyclohexene (17)	1,3-Dimethylcyclohexene (18)	1,3-Dimethylcyclohexene (19)	1,3-Dimethylcyclohexene (20)	1,3-Dimethylcyclohexene (21)	1,3-Dimethylcyclohexene (22)	1,3-Dimethylcyclohexene (23)	1,3-Dimethylcyclohexene (24)	1,3-Dimethylcyclohexene (25)	1,3-Dimethylcyclohexene (26)	1,3-Dimethylcyclohexene (27)	1,3-Dimethylcyclohexene (28)	1,3-Dimethylcyclohexene (29)	1,3-Dimethylcyclohexene (30)	1,3-Dimethylcyclohexene (31)	1,3-Dimethylcyclohexene (32)	1,3-Dimethylcyclohexene (33)	1,3-Dimethylcyclohexene (34)	1,3-Dimethylcyclohexene (35)	1,3-Dimethylcyclohexene (36)	1,3-Dimethylcyclohexene (37)	1,3-Dimethylcyclohexene (38)	1,3-Dimethylcyclohexene (39)	1,3-Dimethylcyclohexene (40)	1,3-Dimethylcyclohexene (41)	1,3-Dimethylcyclohexene (42)	1,3-Dimethylcyclohexene (43)	1,3-Dimethylcyclohexene (44)	1,3-Dimethylcyclohexene (45)	1,3-Dimethylcyclohexene (46)	1,3-Dimethylcyclohexene (47)	1,3-Dimethylcyclohexene (48)	1,3-Dimethylcyclohexene (49)	1,3-Dimethylcyclohexene (50)	1,3-Dimethylcyclohexene (51)	1,3-Dimethylcyclohexene (52)	1,3-Dimethylcyclohexene (53)	1,3-Dimethylcyclohexene (54)	1,3-Dimethylcyclohexene (55)	1,3-Dimethylcyclohexene (56)	1,3-Dimethylcyclohexene (57)	1,3-Dimethylcyclohexene (58)	1,3-Dimethylcyclohexene (59)	1,3-Dimethylcyclohexene (60)	1,3-Dimethylcyclohexene (61)	1,3-Dimethylcyclohexene (62)	1,3-Dimethylcyclohexene (63)	1,3-Dimethylcyclohexene (64)	1,3-Dimethylcyclohexene (65)	1,3-Dimethylcyclohexene (66)	1,3-Dimethylcyclohexene (67)	1,3-Dimethylcyclohexene (68)	1,3-Dimethylcyclohexene (69)	1,3-Dimethylcyclohexene (70)	1,3-Dimethylcyclohexene (71)	1,3-Dimethylcyclohexene (72)	1,3-Dimethylcyclohexene (73)	1,3-Dimethylcyclohexene (74)	1,3-Dimethylcyclohexene (75)	1,3-Dimethylcyclohexene (76)	1,3-Dimethylcyclohexene (77)	1,3-Dimethylcyclohexene (78)	1,3-Dimethylcyclohexene (79)	1,3-Dimethylcyclohexene (80)	1,3-Dimethylcyclohexene (81)	1,3-Dimethylcyclohexene (82)	1,3-Dimethylcyclohexene (83)	1,3-Dimethylcyclohexene (84)	1,3-Dimethylcyclohexene (85)	1,3-Dimethylcyclohexene (86)	1,3-Dimethylcyclohexene (87)	1,3-Dimethylcyclohexene (88)	1,3-Dimethylcyclohexene (89)	1,3-Dimethylcyclohexene (90)	1,3-Dimethylcyclohexene (91)	1,3-Dimethylcyclohexene (92)	1,3-Dimethylcyclohexene (93)	1,3-Dimethylcyclohexene (94)	1,3-Dimethylcyclohexene (95)	1,3-Dimethylcyclohexene (96)	1,3-Dimethylcyclohexene (97)	1,3-Dimethylcyclohexene (98)	1,3-Dimethylcyclohexene (99)	1,3-Dimethylcyclohexene (100)	1,3-Dimethylcyclohexene (101)	1,3-Dimethylcyclohexene (102)	1,3-Dimethylcyclohexene (103)	1,3-Dimethylcyclohexene (104)	1,3-Dimethylcyclohexene (105)	1,3-Dimethylcyclohexene (106)	1,3-Dimethylcyclohexene (107)	1,3-Dimethylcyclohexene (108)	1,3-Dimethylcyclohexene (109)	1,3-Dimethylcyclohexene (110)	1,3-Dimethylcyclohexene (111)	1,3-Dimethylcyclohexene (112)	1,3-Dimethylcyclohexene (113)	1,3-Dimethylcyclohexene (114)	1,3-Dimethylcyclohexene (115)	1,3-Dimethylcyclohexene (116)	1,3-Dimethylcyclohexene (117)	1,3-Dimethylcyclohexene (118)	1,3-Dimethylcyclohexene (119)	1,3-Dimethylcyclohexene (120)	1,3-Dimethylcyclohexene (121)	1,3-Dimethylcyclohexene (122)	1,3-Dimethylcyclohexene (123)	1,3-Dimethylcyclohexene (124)	1,3-Dimethylcyclohexene (125)	1,3-Dimethylcyclohexene (126)	1,3-Dimethylcyclohexene (127)	1,3-Dimethylcyclohexene (128)	1,3-Dimethylcyclohexene (129)	1,3-Dimethylcyclohexene (130)	1,3-Dimethylcyclohexene (131)	1,3-Dimethylcyclohexene (132)	1,3-Dimethylcyclohexene (133)	1,3-Dimethylcyclohexene (134)	1,3-Dimethylcyclohexene (135)	1,3-Dimethylcyclohexene (136)	1,3-Dimethylcyclohexene (137)	1,3-Dimethylcyclohexene (138)	1,3-Dimethylcyclohexene (139)	1,3-Dimethylcyclohexene (140)	1,3-Dimethylcyclohexene (141)	1,3-Dimethylcyclohexene (142)	1,3-Dimethylcyclohexene (143)	1,3-Dimethylcyclohexene (144)	1,3-Dimethylcyclohexene (145)	1,3-Dimethylcyclohexene (146)	1,3-Dimethylcyclohexene (147)	1,3-Dimethylcyclohexene (148)	1,3-Dimethylcyclohexene (149)	1,3-Dimethylcyclohexene (150)	1,3-Dimethylcyclohexene (151)	1,3-Dimethylcyclohexene (152)	1,3-Dimethylcyclohexene (153)	1,3-Dimethylcyclohexene (154)	1,3-Dimethylcyclohexene (155)	1,3-Dimethylcyclohexene (156)	1,3-Dimethylcyclohexene (157)	1,3-Dimethylcyclohexene (158)	1,3-Dimethylcyclohexene (159)	1,3-Dimethylcyclohexene (160)	1,3-Dimethylcyclohexene (161)	1,3-Dimethylcyclohexene (162)	1,3-Dimethylcyclohexene (163)	1,3-Dimethylcyclohexene (164)	1,3-Dimethylcyclohexene (165)	1,3-Dimethylcyclohexene (166)	1,3-Dimethylcyclohexene (167)	1,3-Dimethylcyclohexene (168)	1,3-Dimethylcyclohexene (169)	1,3-Dimethylcyclohexene (170)	1,3-Dimethylcyclohexene (171)	1,3-Dimethylcyclohexene (172)	1,3-Dimethylcyclohexene (173)	1,3-Dimethylcyclohexene (174)	1,3-Dimethylcyclohexene (175)	1,3-Dimethylcyclohexene (176)	1,3-Dimethylcyclohexene (177)	1,3-Dimethylcyclohexene (178)	1,3-Dimethylcyclohexene (179)	1,3-Dimethylcyclohexene (180)	1,3-Dimethylcyclohexene (181)	1,3-Dimethylcyclohexene (182)	1,3-Dimethylcyclohexene (183)	1,3-Dimethylcyclohexene (184)	1,3-Dimethylcyclohexene (185)	1,3-Dimethylcyclohexene (186)	1,3-Dimethylcyclohexene (187)	1,3-Dimethylcyclohexene (188)	1,3-Dimethylcyclohexene (189)	1,3-Dimethylcyclohexene (190)	1,3-Dimethylcyclohexene (191)	1,3-Dimethylcyclohexene (192)	1,3-Dimethylcyclohexene (193)	1,3-Dimethylcyclohexene (194)	1,3-Dimethylcyclohexene (195)	1,3-Dimethylcyclohexene (196)	1,3-Dimethylcyclohexene (197)	1,3-Dimethylcyclohexene (198)	1,3-Dimethylcyclohexene (199)	1,3-Dimethylcyclohexene (200)	1,3-Dimethylcyclohexene (201)	1,3-Dimethylcyclohexene (202)	1,3-Dimethylcyclohexene (203)	1,3-Dimethylcyclohexene (204)	1,3-Dimethylcyclohexene (205)	1,3-Dimethylcyclohexene (206)	1,3-Dimethylcyclohexene (207)	1,3-Dimethylcyclohexene (208)	1,3-Dimethylcyclohexene (209)	1,3-Dimethylcyclohexene (210)	1,3-Dimethylcyclohexene (211)	1,3-Dimethylcyclohexene (212)	1,3-Dimethylcyclohexene (213)	1,3-Dimethylcyclohexene (214)	1,3-Dimethylcyclohexene (215)	1,3-Dimethylcyclohexene (216)	1,3-Dimethylcyclohexene (217)	1,3-Dimethylcyclohexene (218)	1,3-Dimethylcyclohexene (219)	1,3-Dimethylcyclohexene (220)	1,3-Dimethylcyclohexene (221)	1,3-Dimethylcyclohexene (222)	1,3-Dimethylcyclohexene (223)	1,3-Dimethylcyclohexene (224)	1,3-Dimethylcyclohexene (225)	1,3-Dimethylcyclohexene (226)	1,3-Dimethylcyclohexene (227)	1,3-Dimethylcyclohexene (228)	1,3-Dimethylcyclohexene (229)
125	0.8021 ^a	1.4440 ^a	1.0430	95	119	42																																																																																																																																																																																																																																		
127	0.8006	1.4487	1.0484	95	119	41																																																																																																																																																																																																																																		
127	0.8020	1.4470	1.0460	98	122	16																																																																																																																																																																																																																																		
127	0.8070 ^a	1.4437	1.0452	95	119	18																																																																																																																																																																																																																																		
127	0.8004 ^a	1.4446	1.0444	94	117	18																																																																																																																																																																																																																																		
127	0.8041	1.4478	1.0462	158																																																																																																																																																																																																																																		
127	0.8034	1.4476	1.0460	41																																																																																																																																																																																																																																		
132	0.8141	1.4506	1.0436	100																																																																																																																																																																																																																																		
134	0.8034	1.4441	1.0424	145																																																																																																																																																																																																																																		
136	0.8008 ^a	1.4520	1.0466	97	117	186																																																																																																																																																																																																																																		
136	0.8264 ^a	1.4588 ^a	1.0454	100	121	18																																																																																																																																																																																																																																		
138	0.824	1.4578	1.046	152																																																																																																																																																																																																																																		
138	0.8070 ^a	1.4448 ^a	1.0413	97	118	14																																																																																																																																																																																																																																		
139	0.8218	1.4561	1.0452	151																																																																																																																																																																																																																																		
139	0.789	1.4369	1.0424	151																																																																																																																																																																																																																																		
140	0.8032 ^a	1.4488 ^a	1.0472	97	120	47																																																																																																																																																																																																																																		
140	0.8051 ^a	1.4460 ^a	1.0435	97	117	14 av.																																																																																																																																																																																																																																		
140	0.7983 ^a	1.4459 ^a	1.0468	97	121	18																																																																																																																																																																																																																																		
144	0.8082	1.4469	1.0438	76																																																																																																																																																																																																																																		
145	0.8045	1.4479	1.0456	94	117	8, 4																																																																																																																																																																																																																																		
145	0.805	1.448	1.045	41																																																																																																																																																																																																																																		
145	0.855	1.474	1.046	167																																																																																																																																																																																																																																		
149	0.8238	1.4562	1.0444	96	117	14 av.																																																																																																																																																																																																																																		
150	0.8132	1.4536	1.0470	99	120	18																																																																																																																																																																																																																																		
150	0.8271 ^a	1.4593 ^a	1.0458	94																																																																																																																																																																																																																																		
151	0.812	1.4528	1.0468	158																																																																																																																																																																																																																																		
152	0.8091	1.4510	1.0465	94	116	78																																																																																																																																																																																																																																		
152	0.813	1.4544	1.0479	158																																																																																																																																																																																																																																		
153	0.828	1.4594	1.0454	158																																																																																																																																																																																																																																		
154	0.8138	1.4519	1.0450	16 av.																																																																																																																																																																																																																																		
156	0.8263	1.4593	1.0462	96	116	10																																																																																																																																																																																																																																		
156	0.824	1.4578	1.0458	158																																																																																																																																																																																																																																		
157	0.830	1.4630	1.048	158																																																																																																																																																																																																																																		
164	0.8113 ^a	1.4523 ^a	1.0467	97	119	47																																																																																																																																																																																																																																		
166	0.8169 ^a	1.4564 ^a	1.0485	98	120	4																																																																																																																																																																																																																																		
168	0.8289	1.4625	1.0480																																																																																																																																																																																																																																		
169	0.8130 ^a	1.4543 ^a	1.0478	94	116	47, 155																																																																																																																																																																																																																																		
173	0.813	1.4533	1.0468	158																																																																																																																																																																																																																																		
173	0.814	1.4546	1.0476	158																																																																																																																																																																																																																																		
176	0.8230 ^a	1.4554 ^a	1.0439	150																																																																																																																																																																																																																																		
177	0.830	1.4627	1.0477	158																																																																																																																																																																																																																																		
182	0.826	1.4591	1.0461	158																																																																																																																																																																																																																																		
182	0.813 ^a	1.4533 ^a	1.0468	94	116	47 av.																																																																																																																																																																																																																																		
185	0.810	1.4530	1.0480	158																																																																																																																																																																																																																																		
195	0.818	1.4574	1.0484	158																																																																																																																																																																																																																																		
195	0.824	1.4596	1.0476	158																																																																																																																																																																																																																																		
197	0.816	1.4558	1.0478	158																																																																																																																																																																																																																																		
198	0.831	1.4637	1.0482	158																																																																																																																																																																																																																																		
204	0.829	1.4605	1.0460	158																																																																																																																																																																																																																																		
219	0.832	1.4646	1.0486	158																																																																																																																																																																																																																																		
78 at 10 mm.	0.8388 ^a	1.4644	1.0450	94	112	181																																																																																																																																																																																																																																		
...	0.989	1.5385	1.0425	54																																																																																																																																																																																																																																		

^a Calculated from some other temperature than 20° C.

TABLE VIII. PHYSICAL CONSTANTS OF AROMATICS (Concluded)

Approximate Boiling Point °C.	d ₄ ^{20°}	n _D ^{20°}	Refractive Index at 20°	Dispersion × 10 ⁴ F-C	References																																																
						1,3-Dimethyl-5-ethylbenzene	1,4-Dimethyl-2-ethylbenzene	1,5-Dimethyl-2-ethylbenzene	neo-Pentylbenzene	1,1-Diethyl-4-ethylbenzene	1,2-Dimethyl-1,4-ethylbenzene	3-Methyl-1-butylbenzene	4-Methyl-1-butylbenzene	1-Methyl-4-tert-butylbenzene	sec-Amylbenzene	1-Methyl-1-butylbenzene	1,2,3,5-Tetramethylbenzene (isodurene)	1-Ethyl-4-isopropylbenzene	1-Methyl-4-sec-butylbenzene	1-Methyl-3-n-butylbenzene	1-Methyl-4-n-butylbenzene	1-Methyl-3,5-diethylbenzene	1-Methyl-2-n-butylbenzene	1,2-Dimethyl-4-isopropylbenzene	1-Methyl-3,5-diethylbenzene	n-Amylbenzene	1,2-Diethyl-4-propylbenzene	1-Ethyl-4-propylbenzene	1,2,3,4-Tetramethylbenzene	3,3-Dimethyl-1-propylbenzene	1-Methyl-3-(2,2-dimethylpropyl)-benzene	1-Disopropylbenzene	1-Methyl-4-isobutylbenzene	1,3,5-Trimethyl-2-ethylbenzene	1,2,5-Trimethyl-4-ethylbenzene	1-Propyl-4-isopropylbenzene	1-Methyl-2-ethyl-4-isopropylbenzene	1-Methyl-5-ethyl-2-propylbenzene	1,3,5-Trimethylbenzene	1-Methyl, 3,5-diisopropylbenzene	x,x'-Triethylbenzene	(2,3-Dimethyl)butylbenzene	1,2,4-Triethylbenzene	n-Hexylbenzene	1,3,5-Trimethyl-2-n-propylbenzene	1-Butyl-4-isopropylbenzene	1,2,4-Trimethyl-5-isopropylbenzene	1-Methyl-x-x'-diisopropylbenzene	1-Methyl-2-propyl-4-isopropylbenzene	1,2,4-Trimethyl-5-n-propylbenzene	1,1,1-Triethyltoluene	1-Methyl-2,6-diisopropylbenzene	x-tert-Butyl-m-cymene
185	0.861	1.5013 ^a	1.0612	172																																															
185	0.8802 ^a	1.5013 ^a	1.0612	80																																															
186	0.8743 ^a	1.5015 ^a	1.0644	43																																															
186	0.8565	1.4876	1.0594	43																																															
187	0.8717	1.4969	1.0616	80, 70																																															
188	0.8739	1.5027	1.0658	43																																															
189	0.8642	1.4953	1.0632	43																																															
189	0.8704	1.4927 ^a	1.0613	139	161	58, 80																																															
190	0.8668 ^a	1.4947 ^a	1.0616	7																																															
190	0.8616	1.4924	1.0618	112																																															
193	0.8614	1.4906	1.0599	43																																															
195	0.8584	1.4873	1.0581	43																																															
196	0.8906	1.5104	1.0651	43																																															
197	0.8576 ^a	1.4910 ^a	1.0622	8																																															
197	0.8632	1.4912	1.0596	43																																															
198	0.8612 ^a	1.4924 ^a	1.0618	140	163	109																																															
198	0.8636	1.4940	1.0622	43																																															
199	0.8700	1.4957	1.0612	43																																															
200	0.8690 ^a	1.4957	1.0612	109																																															
200	0.8700 ^a	1.4980 ^a	1.0627	143	164	79																																															
201	0.870	1.4884	1.0593	41																																															
201	0.8582	1.4884	1.0593	43																																															
202	0.8642	1.4954	1.0633	151	175	18																																															
203	0.8662	1.4954	1.0633	43																																															
203	0.8662	1.4954	1.0633	43																																															
203	0.8662	1.4954	1.0633	43																																															
203	0.8662	1.4954	1.0633																																																

TABLE VII. PHYSICAL PROPERTIES OF UNSATURATED CYCLICS WITH TWO CONJUGATED DOUBLE BONDS

	Approximate Boiling Point °C.	d ₄ ^{20°}	n _D ^{20°}	Refractivity Intercept at 20°	Dispersion $\frac{F-C}{d}$ × 10 ⁴	References
Cyclopentadiene	40	0.8026 ^a	1.4429 ^a	1.0416	132	164
Cyclohexadiene (1,3)	80	0.8405	1.4750	1.0548	...	6, 8, 47
1-Methylcyclohexadiene (2,4)	101	0.8273 ^a	1.4674 ^a	1.0537	...	63, 165
5,5-Dimethylcyclohexadiene (1,3)	111	0.8113 ^a	1.4996 ^a	1.0666	160	185
Cycloheptadiene (1,3)	121	0.8660 ^a	1.4996 ^a	1.0666	160	185
1,5-Dimethylcyclohexadiene (1,3)	127	0.821	1.471	1.061	...	41
1,2-Dimethylcyclohexadiene (2,6)	136	0.8521	1.4895	1.0632	...	20
1,3-Dimethylcyclohexadiene (1,3)	136	0.8373	1.4856	1.0670	...	71, 118
1,4-Dimethylcyclohexadiene (1,3)	136	0.8330 ^a	1.4800 ^a	1.0635	...	5, 11, 126
1-Methyl-4-ethylcyclohexadiene (1,3)	161	0.8379 ^a	1.4823 ^a	1.0634	...	5, 11, 126
1-Methyl-4-isopropylcyclohexadiene (1,3)	176	0.8350 ^a	1.4785 ^a	1.0610	...	9, 11, 114

^a Value calculated from some temperature other than 20° C.

TABLE VIII. PHYSICAL CONSTANTS OF AROMATICS

	Approximate Boiling Point °C.	d ₄ ^{20°}	n _D ^{20°}	Refractivity Intercept at 20°	Dispersion $\frac{F-C}{d}$ × 10 ⁴	References
Benzene	80	0.8788	1.5012	1.0618	166	189
Toluene	111	0.8670	1.4969	1.0633	160	185
Ethylbenzene	136	0.8669	1.4959	1.0624	153	176
<i>p</i> -Xylene	138	0.8610 ^a	1.4901 ^a	1.0656	158	183
<i>m</i> -Xylene	144	0.8611	1.4905	1.0650	159	181
<i>o</i> -Xylene	153	0.8620 ^a	1.4922 ^a	1.0612	148	172
Isopropylbenzene	159	0.8618	1.4920	1.0611	145	168
<i>m</i> -Methylethylbenzene	162	0.8673 ^a	1.4975 ^a	1.0639	153	177
<i>p</i> -Methylethylbenzene	162	0.8619 ^a	1.4943 ^a	1.0634	150	174
<i>o</i> -Methylethylbenzene	165	0.8807 ^a	1.5041 ^a	1.0638	155	170
1,3,5-Trimethylbenzene (mesitylene)	165	0.8653	1.4990 ^a	1.0663	154	179
<i>tert</i> -Butylbenzene	169	0.8669	1.4925	1.0591	...	43
1,2,4-Trimethylbenzene (pseudocumene)	169	0.8762 ^a	1.5048 ^a	1.0667	150	171
Isobutylbenzene	170	0.8664 ^a	1.4926 ^a	1.0594	140	161
1-Methyl-2- <i>tert</i> -butylbenzene	171	0.8664 ^a	1.4929	1.0594	140	161
<i>sec</i> -Butylbenzene	174	0.8623	1.4901	1.0589	146	167
1-Methyl-2-isopropylbenzene (<i>o</i> -cymene)	175	0.8759 ^a	1.5003 ^a	1.0624	...	43
1-Methyl-3-isopropylbenzene (<i>m</i> -cymene)	176	0.8605 ^a	1.4925 ^a	1.0623	144	167
1-Methyl-4-isopropylbenzene (<i>p</i> -cymene)	177	0.8569	1.4906	1.0622	144	168
1,2,3-Trimethylbenzene (hemimellitene)	176	0.8951	1.5139 ^a	1.0664	157	176
1,2-Diethylbenzene	177	0.8811	1.5036	1.0630	148	168
1,3-Diethylbenzene	181	0.8617 ^a	1.4955 ^a	1.0647	146	168
1-Methyl-3-propylbenzene	182	0.8625 ^a	1.4951 ^a	1.0639	146	169
<i>n</i> -Butylbenzene	183	0.8606	1.4936	1.0633	148	171
1-Methyl-4-propylbenzene	183	0.8606 ^a	1.4954 ^a	1.0651	137	159
1,4-Diethylbenzene	183	0.8649 ^a	1.4973 ^a	1.0649	145	168
1-Methyl-2-propylbenzene	184	0.8737 ^a	1.4995 ^a	1.0627	...	3

^a Calculated from some other temperature than 20° C.

TABLE IX. DICYCLIC SATURATED HYDROCARBONS

	Approximate Boiling Point °C.	d ₄ ^{20°}	n _D ^{20°}	Refractivity Intercept at 20°	Dispersion $\frac{F-C}{d}$ × 10 ⁴	References
3,3-Dimethyl-dicyclo-(0,1,3)-hexane	115	0.8043	1.4021	1.0337	...	20
Saturated dicyclic C ₈ H ₁₄	132	0.7972	1.4346	1.0360	79	99
Dicyclo-(0,x,x)-octane	140	0.8604	1.4615	1.0313	...	20
2,6,6-Trimethyldicyclo-(0,1,3)-heptane	141	0.8223	1.4465	1.0355	...	20
2,2-Dimethyldicyclo-(1,2,2)-heptane (camphenilene)	143	0.8546	1.4555	1.0282	...	20
1,3,3-Trimethyldicyclo-(1,2,2)-heptane (fenchane)	149	0.8316	1.4462	1.0304	...	20
6,6-Dimethyldicyclo-(1,1,3)-heptane (nopinane)	149	0.8630	1.4641	1.0326	...	20
2,3-Dimethyldicyclo-(1,2,2)-heptane (santane)	151	0.8700	1.4630	1.0280	...	41
4-Methyl-1-isopropyl-dicyclo-(0,1,3)-hexane (sabinane)	157	0.8163	1.4393	1.0312	...	20
Dicyclohexane	161	0.8521	1.4626	1.0366	82	93
Methylcyclohexane	163	0.8784	1.4705	1.0313	...	47
2,7,7-Trimethyldicyclo-(1,2,3)-heptane (isobornylane)	164	0.8579	1.4590	1.0300	...	20
2,6,6-Trimethyldicyclo-(1,1,3)-heptane (pinane), <i>trans</i>	165	0.8501	1.4585	1.0335	...	41
2,6,6-Trimethyldicyclo-(1,1,3)-heptane (pinane), <i>cis</i>	168	0.8562	1.4624	1.0343	...	41
3,7,7-Trimethyldicyclo-(0,1,4)-heptane (carane)	170	0.8410	1.4562	1.0362	...	41
1-Methyldicyclo-(1,3,3)-nonane	178	0.8416	1.4529	1.0321	...	20
Decahydronaphthalene, <i>trans</i>	185	0.8699	1.4697	1.0329	...	20
Decahydronaphthalene (mixed isomers)	192	0.8895	1.4765	1.0318	88	95
Decahydronaphthalene, <i>cis</i>	194	0.8963	1.4811	1.0329	...	20
Dicyclopentylmethane	207	0.8568	1.4642	1.0360	...	20
9 Methyl-3-isopropyl-dicyclo-(1,3,3)-nonane	233	0.8643	1.4660	1.0338	...	20
Dicyclohexylmethane	252	0.8763	1.4771	1.0390	85	97

TABLE X. TRICYCLIC SATURATED HYDROCARBONS

	Approximate Boiling Point °C.	d ₄ ^{20°}	n _D ^{20°}	Refractivity Intercept at 20°	Dispersion $\frac{F-C}{d}$ × 10 ⁴	References
2,2,5-Trimethyl-3,6-methylene-dicyclo-(0,1,3)-hexane (cyclofenchane)	145	0.8600	1.4522	1.0222	87	101
Nortricyclohexanone	184	0.885	1.4686	1.0261	...	41
Dodecahydrofluorene	253	0.9190	1.485	1.026	...	20
Tricyclodecane	...	0.9500	1.4958	1.0208	...	20

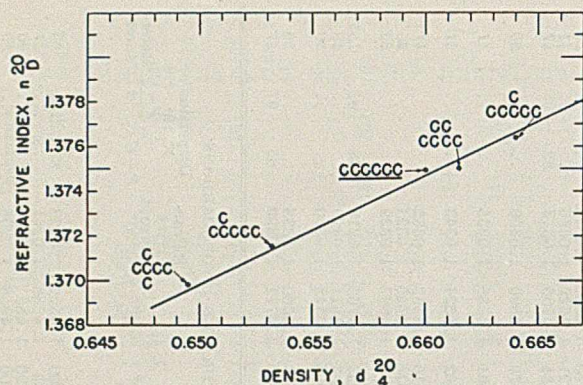


FIGURE 1. REFRACTIVE INDEX AND DENSITY OF ISOMERIC HEXANES

Densities and refractive indices are tabulated as d_4^{20} and n_D^{20} . It is the well considered opinion (156) of the authors that 20°C . should be adhered to as the standard reference temperature for recording and tabulating refractive index and density data for both high and low molecular weight hydrocarbons which are liquid at 20°C . As is well known, some investigators still report densities and indices at different temperatures and much of the older work was reported at the most diverse temperatures. In the case of the old style tabulations such as Landolt-Börnstein (89) and the Annual Tables of Physical Constants (97) the compilers, lacking an adequate basis for correction, were compelled to tabulate data at whatever temperatures were in the original literature. This made correlation almost impossible. For the more common hydrocarbons, temperature coefficients are becoming known. This has permitted the more recent compilations, such as those in the International Critical Tables (69) and the Science of Petroleum (41) and the unusually complete tabulations of Egloff and von Grosse (43, 60), to give data at 20°C . At best, data converted to 20°C . are substitutes for values actually determined at the standard temperature. Therefore, it is to be hoped that all workers in the field of hydrocarbon research will adopt this reference temperature. In the case of high-melting compounds it is suggested that 80°C . be adopted as a secondary reference temperature since very few hydrocarbons melting above 80°C . are encountered, and since 80°C . has been used both by Ferris and co-workers (51) and by Katz (72).

Dispersions are given for the $F - C$ (or $H_\beta - H_\alpha$) interval. The refractive index for the C or H_α line and the F or H_β line may be obtained by the following equations based on the Cauchy formula:

$$n_C^{20} = n_F^{20} - 0.292 (n_F - n_C) \quad (1)$$

$$n_F^{20} = n_C^{20} + 0.708 (n_F - n_C) \quad (2)$$

Except in a few cases the dispersion data tabulated are from the same reference as given for the density and refractive index data; therefore separate literature references have not been given for any dispersion data. If it be desired to convert the $F - C$ dispersion to dispersion for any other spectrum interval $X - Z$, then one may use the equation

$$(n_X - n_Z) = (n_F - n_C) \frac{(1/\lambda_X^2 - 1/\lambda_Z^2)}{1.9095}$$

Values for the wave length λ and $1/\lambda^2$ for the common spectral lines are given in Table XI.

In addition to boiling point, density, refractive index, and dispersion, two derived constants are tabulated—namely, the refractivity intercept $n - d/d$ of Kurtz and Ward (88) and the specific dispersion $(F - C)/d$ (155). The refractivity intercept is extremely useful in many problems relating to hydro-

carbon analysis and identification. For example, the low values of the refractivity intercepts for the naphthenes are especially helpful in showing the presence of such compounds in hydrocarbon mixtures. Again, it may frequently be used for the quantitative analysis of hydrocarbon mixtures either as a part of a scheme of analysis such as described by Kurtz and Headington (87) for complex mixtures or alone for simpler mixtures, such, for example, as a mixture of conjugated and nonconjugated diolefins or of aromatics and naphthenes. The specific dispersion is also very valuable, since it is practically constant for all saturated hydrocarbons whether cyclic or noncyclic and is useful in determining aromatics.

TABLE XI. EXTRAPOLATION AND INTERPOLATION OF REFRACTIVE INDICES

Spectrum Line	Wave Length λ Å.	$\frac{1}{\lambda^2} \times 10^{-8}$
C or H_α	6563	2.322
D_1	5896	2.877
D	5893	2.880
D_2	5890	2.883
$H_e f$	5876	2.900
Hg green	5461	3.353
$H_e v$	5016	3.975
F or H_β	4861	4.231
$H_e c$	4713	4.502
$H_e i$	4472	5.000
g (Hg blue)	4358	5.265
G' or H	4341	5.307

Graphs of refractivity intercept versus boiling point give peaks at those boiling points where mono- or diolefins or aromatics predominate and troughs at those boiling points where naphthenes predominate. If both naphthenes and aromatics are present in the same cut, the presence of the latter can be shown by the high specific dispersion.

Relationship between Structure and Physical Properties of Hydrocarbon Isomers

It is a tribute to the skill and patience of organic chemists that such a mass of data as is summarized in Tables I to X can be collected. Years ago, the late T. W. Richards (122) was interested in correlating such data, but was hampered by the lack of accurate values for a sufficient number of hydrocarbons, by the existing state of the art on the synthesis of hydrocarbons and, in particular, by the lack of established generalizations that now permit sifting data to reject values that are obviously out of line and to select those that must be at least reasonably accurate. For example, it is clear now that the physical properties of many of the octanes synthesized for Richards by Clarke (35) were not reliable. Recent data by Boord (25), Maman (96), Smittenberg, Hoog, and Henkes (139), and Whitmore and Laughlin (163) confirm for the octanes generalizations that have been drawn from other work for the isomers of the lower members of the series. Such generalizations show the inadequacy of the older octane data. The point is illustrated by a comparison of the data for two of the isomers, the average refractivity intercept for seventeen octanes being 1.0452.

Isomer	d_4^{20}	n_D^{20}	Refractivity Intercept	Reference
2,3-Dimethylhexane	0.7206	1.4098	1.0495	35
	0.7123	1.4013	1.0451	139
2,2,3-Trimethylpentane	0.7173	1.4187	1.0601	35
	0.7173	1.4030	1.0444	163

The high value of the refractivity intercept of many of Clarke's octanes indicates either the presence of olefins or incorrect refractive index data.

Since the paraffins are the simplest series, a study of the effect of structure on the physical properties of isomers should begin there. The papers of Morgan, Carter, and Duck (105)

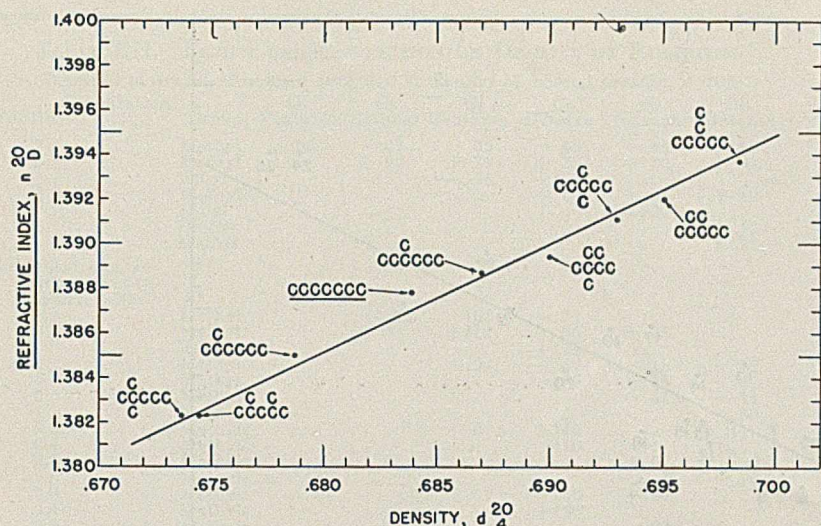


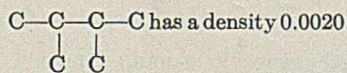
FIGURE 2. REFRACTIVE INDEX AND DENSITY OF ISOMERIC HEPTANES

in 1925 and of Edgar and Calingaert (42) in 1930 placed the study of isomeric paraffins on a relatively sound basis; in fact, a careful consideration of the data of the latter authors for the isomeric heptanes leads to the writers' conclusion (38) that the classic Newton specific refraction equation, $\frac{n^2 - 1}{d}$, accurately represents the relationship between n and d for hydrocarbon isomers.

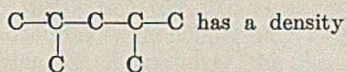
Figures 1, 2, and 3 show the data in the present tabulation for the isomeric hexanes, heptanes, and octanes, the carbon skeleton being indicated and a straight-line curve corresponding to the average Newton specific refraction equation being shown. The close agreement between the experimental data and the curves for the Newton equation is obvious. Graphs for the isomeric nonanes and decanes are similar to those presented.

Among other things, the graphs also strikingly illustrate some of the generalizations of Morgan, Carter, and Duck (105), Edgar and Calingaert (42), and Boord (25). It is clear that substitution that tends to increase the symmetry of the molecule raises the density and index, whereas substitution that tends to make the molecule less compact, decreases both d and n .

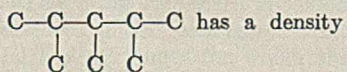
The very large effect of symmetry, or central grouping, is shown not merely by the fact that a perfectly symmetrical hydrocarbon such as 3,3-diethylpentane has a density of 0.0342 higher than that of normal nonane but also by many other comparisons. Thus



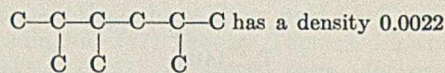
higher than that of the normal isomer, but



0.0094 lower than that of the normal isomer. Again

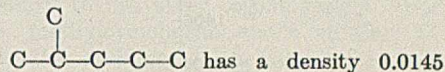


0.0169 higher than that of the normal isomer, but

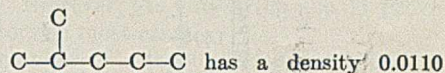


lower than the normal isomer.

Similarly



higher than that of the normal isomer, but



lower than that of the normal isomer.

The relationships are expressed numerically in Table XII. Edgar and Calingaert (42) stated, "It would appear probable, therefore, that approximate values of most of the physical properties of paraffin hydrocarbons can be predicted with reasonable assurance when their structure is known." The steady increase in sound data available now makes it possible to test this statement. For the 6 paraffins from C_5 to C_{10} , the effect of substitution in the 2 position is to lower the density in comparison to the normal isomer by an average of 0.0056 with an average deviation of 0.0007. The average increase in density (in comparison to the normal isomer) by substitution in the 3 position for the five paraffins is 0.0032 with a mean deviation of 0.0005. The degree of approximation of the predictable properties is rapidly approaching the accuracy with which these properties are determined in many laboratories.

It is beyond the scope of the present paper adequately to discuss the effect of structure on the physical properties of isomeric olefins. Figure 4, the data for which are largely from the excellent work of Soday and Boord (142); shows the values for the isomeric heptenes, the curve again corresponding to the Newton equation. Naturally, the conflicting effects of the position of the double bonds and the substituted

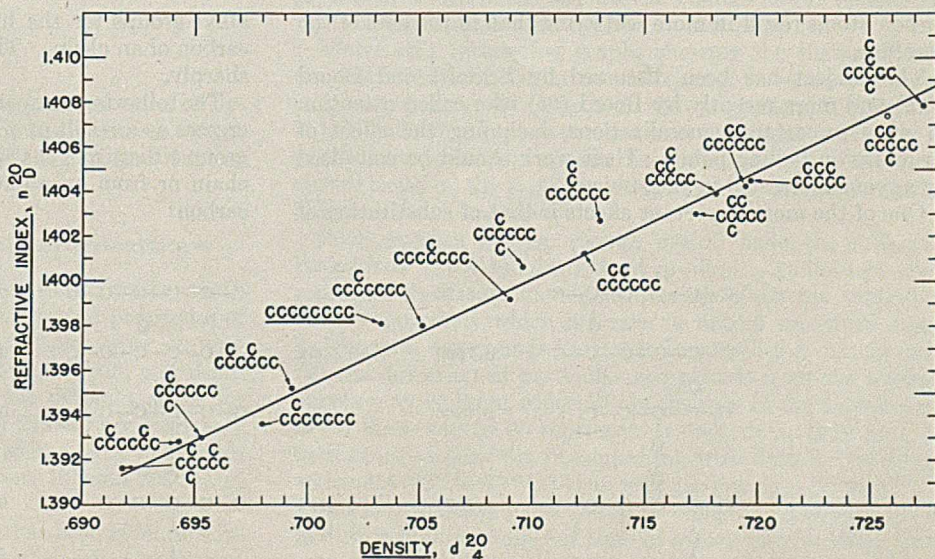


FIGURE 3. REFRACTIVE INDEX AND DENSITY OF ISOMERIC OCTANES

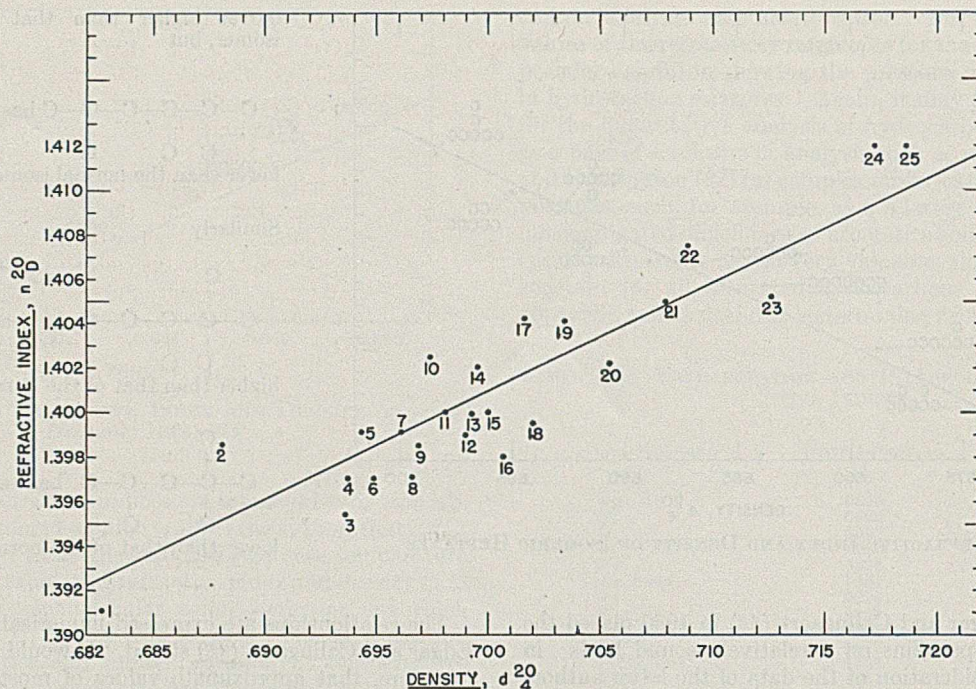
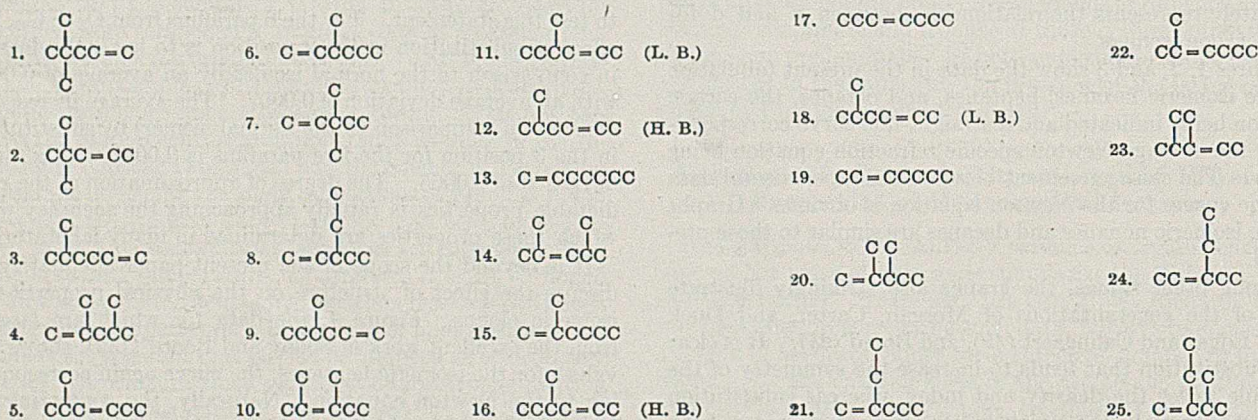


FIGURE 4. REFRACTIVE INDEX AND DENSITY OF ISOMERIC HEPTENES STRUCTURE CORRESPONDING TO NUMBERED POINTS IN FIGURE 4



carbon atoms result in more scattering than in the case of the paraffins.

The subject has been discussed by Schmitt and Boord (129) and more recently by Boord (25) who called attention to some important generalizations, including the effect of structure on boiling point. Their work should be consulted by anyone interested in the subject.

One of the most important effects is that of substitution of

alkyl groups for the hydrogen attached to the unsaturated carbon of an olefin. This raises the physical constants rather sharply.

The following comparisons are interesting in showing the increases as a result of a shift in the position of the substituted group either from the same position at the opposite end of the chain or from an adjacent carbon atom to the unsaturated carbon:

	d_4^{20}	Δ		d_4^{20}	Δ
$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	0.6936	$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	0.6994 ^a
$\begin{array}{c} \text{C} \\ \\ \text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	0.7000	+0.0064	$\begin{array}{c} \text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	0.7120	+0.0126
$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	0.6966	$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	0.6966
$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	0.7079	+0.0113	$\begin{array}{c} \text{C}-\text{C}=\text{C}-\text{C}-\text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	0.7172	0.0206

^a Average of high-boiling and low-boiling isomers.

TABLE XII. EFFECT OF SUBSTITUTION ON DENSITY OF PARAFFINS

Substitution		Densities of branched isomers compared to density of normal paraffin $\times 10^4$					
Position	Group	C ₅ Pentanes	C ₆ Hexanes	C ₇ Heptanes	C ₈ Octanes	C ₉ Nonanes	C ₁₀ Decanes
2	Methyl	-65	-63	-52	-48	-46	-62
3	Methyl	..	+45	+31	+23	+30	+31
	Ethyl	+145	+102
4	Methyl	+62	+65	+19
	Ethyl	+227	..
5	Propyl	+56
	Methyl	+22
2 Methyl plus additional substitution as follows:							
2	Methyl	..	-102	-102	-75
3	Methyl	..	+20	+112	+95	+55	..
	Ethyl	+154
4	Methyl	-94	-35	-18	-60
5	Methyl	-85	-35	..
6	Methyl	-51	-14
7	Methyl	-60
2,3	Methyls	+61	+145
2,4	Methyls	-110
2,5	Methyls	-99	..
2,6	Methyls	-89
3,3	Methyls	+230	+124	..
3,4	Methyls	+169
3,5	Methyls	-22	..
4,6	Methyls	-106
3 Methyl plus additional substitution as follows:							
3	Methyl	+93	+68
3	Ethyl	+246
4	Methyl	+167
6	Methyl	+60
3 Ethyl plus additional substitution as follows:							
3	Ethyl	342	..

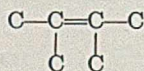
The effect of symmetry, or central grouping, is similar to the effect in the case of the paraffins. Thus,

$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$ has a density 0.0061 higher than that of heptene (1) but

$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ | \quad \quad | \\ \text{C} \quad \quad \text{C} \end{array}$ has a density 0.0046 lower than heptene (1).

Both should be equally affected by the substitution of the hydrogen attached to the unsaturated carbon.

In the case of those olefins in which different factors produce a cumulative effect in the same direction, the change in physical properties is very large. Thus in the case of



with a compact central grouping and with substitution of hydrogen of both the unsaturated carbons, the density is 0.0349 higher than that of hexene (1) or 0.0268 higher than that of hexene (2).

Averaged Data for Classes of Hydrocarbons

The large number of isomers for which data are now available makes it difficult to think in terms of the properties of individual hydrocarbons. In the case of much work on mixtures of hydrocarbons such as those obtained from petroleum by distillation (50, 67), averages for the different series for moderately wide boiling ranges (20° to 30° C.) are extremely valuable. Accordingly, the data in Table I to X have been averaged for seven boiling ranges between 10° and 200° C. in Table XIII.

In selecting the ranges, consideration has been given to convenience in the analysis of liquid hydrocarbon mixtures. The boiling ranges for which the data are averaged are as

follows: 10° to 40° C.; 40° to 70° C.; 70° to 100° C.; 100° to 125° C.; 125° to 150° C.; 150° to 175° C.; 175° to 200° C. These are approximately the same as those used by Kurtz and Headington (87) and by Thomas, Bloch, and Hoekstra (144). In special cases—for example, in mixtures containing a large amount of one compound the boiling point of which is almost identical with a cut point—it may be necessary to use other boiling ranges. For example, methylcyclohexane boils at 100° C. which is the dividing point between cuts 3 and 4; therefore, if much of this compound is present it would be desirable to take cut 3 from 70° to 90° C. and cut 4 from 90° to 120° C. However, the cuts given should prove satisfactory in most cases.

The number of compounds for which boiling point, density, and refractive index data are available is given immediately after the name of the type of compound; the boiling point at 760 mm. density (d_4^{20}), refractive index (n_D^{20}), and refractivity intercept ($n - d/2$) are then listed in order. Following these are "derived dispersion" and "derived specific dispersion." These values were obtained by reading the specific dispersion corresponding to the average boiling point from the graph of specific dispersion vs. boiling point (see below), and then multiplying by the average density. This "derived dispersion," therefore, corresponds to the average density and average refractive index and may be used in connection with Equations 1 and 2 and the Sellmeier-Drude equation (88) to calculate the number and frequency of vibration of the dispersion electrons.

The use of the derived values was made necessary by the fact that the average data for the hydrocarbons for which dispersions have been reported are slightly different from corresponding data for all the known hydrocarbons boiling in the same range.

The latter part of each table presents the actual dispersion data which the authors have been able to tabulate. It is probable that there are more data on dispersion buried in the literature, and it is to be hoped that some one will attempt a more complete tabulation and correlation of dispersion data. Nevertheless it is not believed that future tabulations of dispersion data will make any radical change in the generalizations concerning dispersion given in this paper.

Many very interesting graphs showing the change in the density boiling point relation with change in structure can be prepared, as has previously been shown by the authors (156). It is intended in the present discussion to generalize in so far as possible the properties of each class of compounds; therefore, curves based on the table of averaged properties are presented (Figures 5 to 9, inclusive).

Such average curves, though useful, have the following limitations which should be kept in mind: (1) Because they represent the direct numerical average of all the tabulated data, compounds which are rare in nature are given equal weight with compounds known to be plentiful in nature; and (2) the deviation of particular compounds from the average curves may be large, especially in the case of the naphthenes. Since these curves do represent average data, they may be used more successfully in connection with data for relatively wide cuts (20° to 30° C.) than with narrow cuts (2° to 5° C.), as a more representative group of compounds will be found in a wide boiling range cut than in a very narrow cut. Density, refractive index, and refractivity intercept and dispersion are all additive on a volume per cent basis (156); there-

TABLE XIII. AVERAGE PROPERTIES FOR CUTS OF SPECIFIED BOILING RANGE

Class	Number of Compounds	Boiling Point	d_4^{20}	n_D^{20}	$n - d/2$	Derived Dispersion		Observed Dispersion			
						$F - C$	$(F - C)/d$	Number of compounds	Boiling point	$(F - C) \times 10^4$	$(F - C)/d \times 10^4$
Group 1, Boiling Range 10° to 40° C.											
Noncyclic											
Paraffins	2	32	0.6230	1.3556	1.0442	61.7	99	2	32	62.5	100
Monoolefins	6	32	0.6474	1.3771	1.0534	87.4	135	2	37	88.5	135
Nonconjugated diolefins	1	26	0.6594	1.3880	1.0583	101.5	154
Conjugated diolefins	1	34	0.6805	1.4216	1.0814	153.1	225	1	34	155	225
Monocyclic											
Naphthenes (all)	4	31.5	0.6791	1.3763	1.0368	67.2	99	1	33	72	106
Monoolefins	1	38	0.7105	1.4052	1.0500	83.8	118	1	38
Conjugated diolefins	1	40	0.8026	1.4429	1.0416	128.4	160	1	40	129	160
Group 2, Boiling Range 40° to 70° C.											
Noncyclic											
Paraffins	5	60	0.6575	1.3734	1.0446	65.1	99	5	60	65	99
Monoolefins	14	60	0.6783	1.3909	1.0517	88.2	130	5	65	89	129
Nonconjugated diolefins	4	62	0.6949	1.4095	1.0621	102.1	147	1	60	100	145
Conjugated diolefins	2	56.5	0.7038	1.4352	1.0832	155.5	221	2	56.5	156	221
Monocyclic											
Naphthenes (all)	2	51.5	0.7202	1.3967	1.0367	71.3	99	2	57.5	76	105
Monoolefins	1	44	0.7742	1.4230	1.0359	91.4	118	1	44	92	118
Conjugated diolefins	1	40	0.8026	1.4429	1.0416	128.4	160	1	40	129	160
Group 3, Boiling Range 70° to 100° C.											
Noncyclic											
Paraffins	10	89	0.6866	1.3884	1.0451	68.0	99	10	89	67	98
Monoolefins	27	87	0.7003	1.4012	1.0512	87.5	125	3	91	88	123
Nonconjugated diolefins	3	90	0.7206	1.4228	1.0625	102.3	142	1	92	105	145
Conjugated diolefins	9	80	0.7232	1.4465	1.0849	156.2	216	6	80	165	227
Monocyclic											
Naphthenes (all)	9	86	0.7509	1.4125	1.0371	74.3	99	5	89	75	98
Naphthenes (C ₆ ring only)	2	90.5	0.7744	1.4253	1.0382	76.7	99	2	90.5	78.5	101
Monoolefins	3	86	0.7837	1.4334	1.0417	92.5	118	1	83	97	119
Conjugated diolefins	1	80	0.8405	1.4750	1.0548	148.8	177	1	80	149	177
Aromatics	1	80	0.8789	1.5012	1.0617	166.1	189	1	80	166	189
Group 4, Boiling Range 100° to 125° C.											
Noncyclic											
Paraffins	16	115	0.7096	1.3999	1.0451	70.3	99	10	116	70	100
Monoolefins	13	113	0.7249	1.4236	1.0530	89.2	123	5	121	88	122
Nonconjugated diolefins	3	114	0.7362	1.4327	1.0646	103.1	140
Conjugated diolefins	7	110	0.7451	1.4540	1.0814	156.5	210	3	109	160	215
Monocyclic											
Naphthenes (all)	16	117	0.7714	1.4252	1.0395	76.4	99	11	118	68.5	99
Naphthenes (C ₆ ring only)	8	121.4	0.7785	1.4293	1.0401	77.1	99	6	122	76.8	99.7
Monoolefins	15	116	0.8010	1.4445	1.0441	94.5	118	5	...	93.5	117
Conjugated diolefins	2	111	0.8467	1.4835	1.0602	153.6	184	1	121	160	185
Aromatics	1	111	0.8670	1.4969	1.0633	159.5	184	1	111	160	185
Dicyclic											
Saturated	1	115	0.8043	1.4358	1.0337	79.6	99
Group 5, Boiling Range 125° to 150° C.											
Noncyclic											
Paraffins	12	139	0.7231	1.4071	1.0456	71.6	99	3	140	71	98
Monoolefins	7	142	0.7454	1.4247	1.0520	89.4	120	1	133	90	121
Nonconjugated diolefins	3	143	0.7654	1.4438	1.0611	105.6	138	2	144	106	138
Conjugated diolefins	8	142	0.7623	1.4604	1.0792	157	206	3	143	152	201
Monocyclic											
Naphthenes (all)	20	140	0.7863	1.4331	1.0401	77.8	99	16	139	77	99
Naphthenes (C ₆ ring only)	12	140	0.7895	1.4356	1.0408	78.2	99	9	139	70	99.5
Monoolefins	23	138	0.8125	1.4513	1.0451	95.9	118	11	139	97	119
Conjugated diolefins	4	135	0.8359	1.4815	1.0637	158	189	1	136	162	192
Aromatics	4	139	0.8677	1.4981	1.0643	154.4	178	4	139	157	181
Dicyclic											
Saturated	6	142	0.8382	1.4514	1.0323	83	99	1	132	79	99
Tricyclic											
Saturated	1	145	0.8600	1.4522	1.0222	85	99	1	145	87	101
Group 6, Boiling Range 150° to 175° C.											
Noncyclic											
Paraffins	16	163	0.7348	1.4135	1.0461	72.7	99	6	165	72	99
Monoolefins	7	162	0.7499	1.4286	1.0537	89.2	119	3	161	89	119
Nonconjugated diolefins	6	162	0.7772	1.4475	1.0590	107.2	138	2	165	106	138
Conjugated diolefins	4	165	0.7792	1.4629	1.0734	158.2	203
Monocyclic											
Naphthenes (all)	18	162	0.7974	1.4385	1.0399	78.9	99	9	164	79	99
Naphthenes (C ₆ ring only)	13	164.1	0.8027	1.4413	1.0400	79.5	99	8	165	79.1	99
Monoolefins	14	160	0.8175	1.4557	1.0470	96.5	118	4	159	96	118
Conjugated diolefins	2	169	0.8365	1.4804	1.0622	162	194	2	169	150	169
Aromatics	11	166	0.8679	1.4963	1.0624	149.3	172	10	165	148	170
Dicyclic											
Saturated	7	161	0.8544	1.4593	1.0321	84.6	99	1	163	82	93
Group 7, Boiling Range 175° to 200° C.											
Noncyclic											
Paraffins	4	190	0.7515	1.4229	1.0472	74.4	99	1	195	74	100
Monoolefins	3	186	0.7661	1.4362	1.0532	90.4	118
Monocyclic											
Naphthenes (all)	11	187	0.8037	1.4430	1.0412	79.6	99	1	178	77	97
Naphthenes (C ₆ ring only)	11	187.9	0.8037	1.4430	1.0412	79.6	99	1	178	77	97
Monoolefins	9	187	0.8212	1.4578	1.0472	96.9	118	1	182	94	116
Aromatics	26	189	0.8680	1.4965	1.0625	145.8	168	10	185	145	167
Dicyclic											
Saturated	5	184	0.8677	1.4673	1.0333	85.9	99
Tricyclic											
Saturated	1	184	0.885	1.4688	1.0261	87.6	99

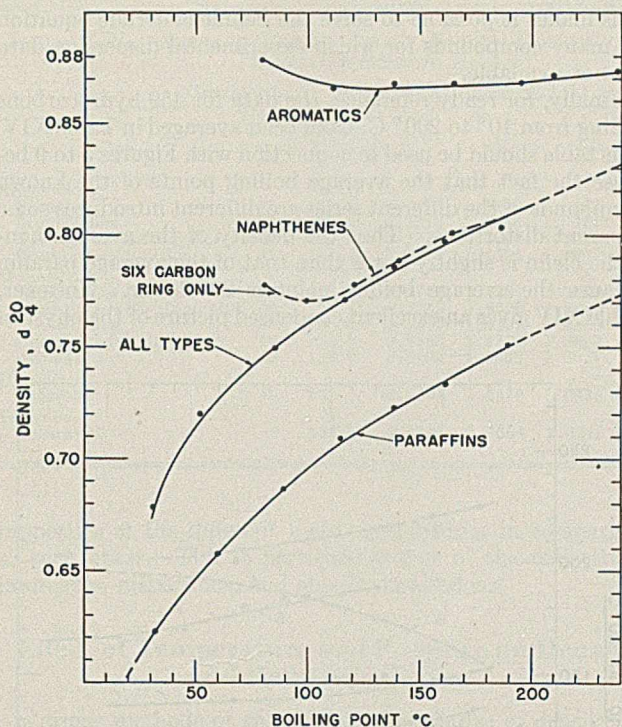


FIGURE 5. DENSITY-BOILING POINT RELATIONSHIP FOR PARAFFINS, NAPHTHENES, AND AROMATICS

fore a direct numerical average of these properties is equivalent to the value which should be obtained on mixing equal volumes of all the compounds averaged. Specific dispersion, on the other hand, is additive on a weight per cent and boiling point approximately on a mole per cent basis. For the relatively narrow cuts concerned in Table XIII the difference between volume per cent, weight per cent, and mole per cent, will be small, but in the case of the general average over the range 10° to 200° C. the distinction must be kept in mind. Fortunately, all the properties needed for solving the Sellmeier-Drude equation are additive on the same basis—namely, the volume per cent basis.

In Figure 5 the densities of the three hydrocarbon series occurring naturally in petroleum are plotted against boiling point. The naphthenes (defined as saturated monocyclic compounds) containing six carbon atoms in the ring are plotted separately in order to bring out the relation between the six-ring saturated cyclics and the aromatics.

Figure 6 for cyclic and noncyclic olefins is drawn on the same scale as Figure 5. It is clear that the noncyclic olefins fall between the paraffins and naphthenes in density and that the cyclic olefins fall between the naphthenes and the aromatics.

Figure 7 for the refractivity intercept *vs.* boiling point shows the small but significant change in refractivity intercept with increase in boiling point. As pointed out in the original discussion (88) of this relationship, the intercept could have been made more constant for the homologous series by using a slope slightly greater than 0.5 in the intercept equation, but since in groups of hydrocarbon isomers the slope is approximately 0.485, a mean slope of 0.5 was chosen. The relatively uniform spacing of the curves for the noncyclic monoolefins, the paraffins, and the one-, two-, and three-ring cyclics suggests a roughly uniform increment for the addition or removal of two hydrogens when conjugation is not involved.

Taking the general average for the range 10° to 200° C. the increments are as follows:

	Increment of Intercept
Monoolefins to paraffins	67
Paraffins to monocyclic saturated	60
Monocyclic to dicyclic saturated	69
Dicyclic to tricyclic saturated	84

As data for only two tricyclic saturated compounds boiling in this range are available, the last increment is admittedly uncertain.

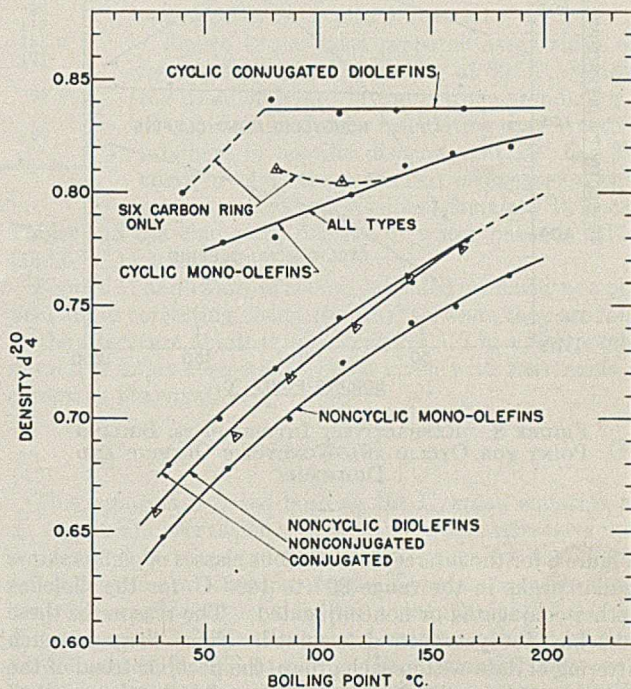


FIGURE 6. RELATION OF DENSITY TO BOILING POINT FOR UNSATURATED COMPOUNDS

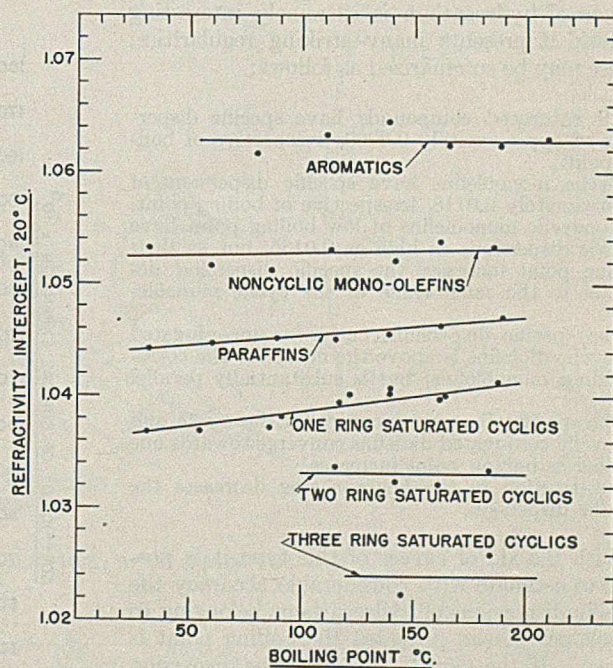


FIGURE 7. REFRACTIVITY INTERCEPT *vs.* BOILING POINT FOR PARAFFINS, NAPHTHENES, AROMATICS, AND NONCYCLIC MONOOLEFINS

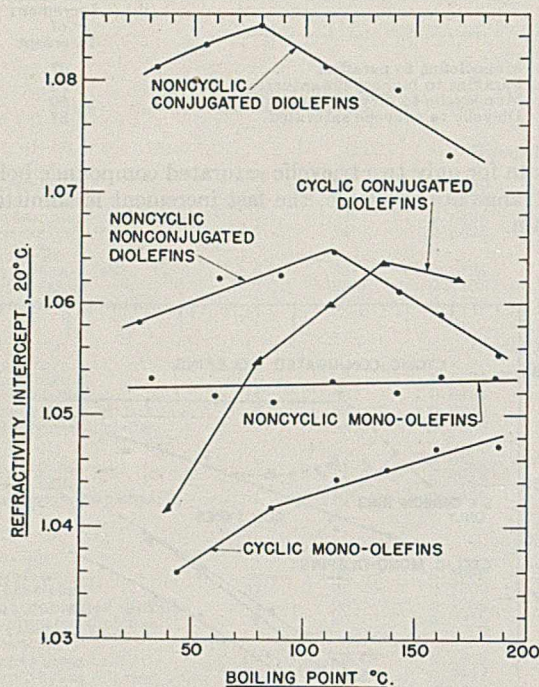


FIGURE 8. REFRACTIVITY INTERCEPT *vs.* BOILING POINT FOR CYCLIC AND NONCYCLIC OLEFINS AND DIOLEFINS

Figure 8 for the intercepts of various classes of olefins shows peculiar peaks in the range 80° to 140° C. for the diolefins whether conjugated or nonconjugated. The reason for these peaks has not yet been determined. Since there is much scattering of data within each group, the peculiar trend of the average curves for the diolefins may possibly be the result of poor data. The authors are, however, inclined to believe that there is some fundamental reason for these peaks and hope to find out just what it is.

Figure 9 for the specific dispersion $(n_F - n_C)/d$ of various classes of hydrocarbon is extremely interesting because it presents many striking regularities. These may be summarized as follows:

All saturated compounds have specific dispersions of approximately 0.0099, irrespective of boiling point.

Cyclic monoolefins have specific dispersions of approximately 0.0118, irrespective of boiling point.

Noncyclic monoolefins of low boiling point have specific dispersions as high as 0.0135, but as their boiling point increases the specific dispersion decreases to the same value as the cyclic monoolefins.

The specific dispersions curve for unconjugated noncyclic diolefins is above the curve for the corresponding monoolefins, but is substantially parallel to it.

The specific dispersions curves for the cyclic and noncyclic conjugated diolefins converge towards one another as boiling point increases.

Substitution in the benzene ring decreases the specific dispersion.

With the aid of curves of this type it is possible to estimate with considerable accuracy the specific dispersions of hydrocarbons belonging to the classes shown, provided the boiling point is known. If the density is known the dispersion can be calculated, and with the aid of Equations 1 and 2 and n_D^{20} it is possible to calculate the refractive index for the *C* and *F* lines.

This makes it possible to solve the Sellmeier-Drude equation for many compounds for which experimental dispersion data are not available.

Finally, for ready reference, the data for 459 hydrocarbons boiling from 10° to 200° C. have been averaged in Table XIV. This table should be used in connection with Figures 5 to 9 because the fact that the average boiling points of the known compounds of the different series are different introduces some apparent distortions. Thus the density of the average noncyclic olefin is slightly lower than that of the average paraffin because the average boiling point is 20° lower. However, Table XIV gives an excellent condensed picture of the physical

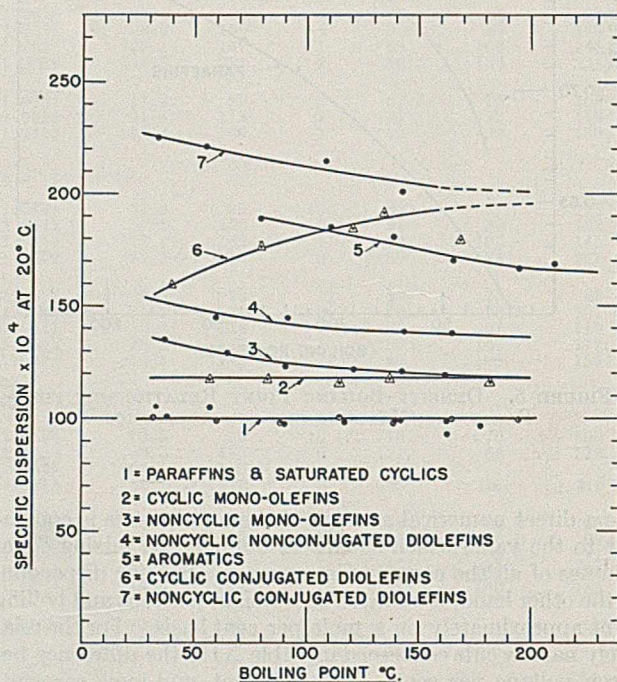


FIGURE 9. RELATION OF SPECIFIC DISPERSION TO BOILING POINT FOR EIGHT SERIES OF HYDROCARBONS

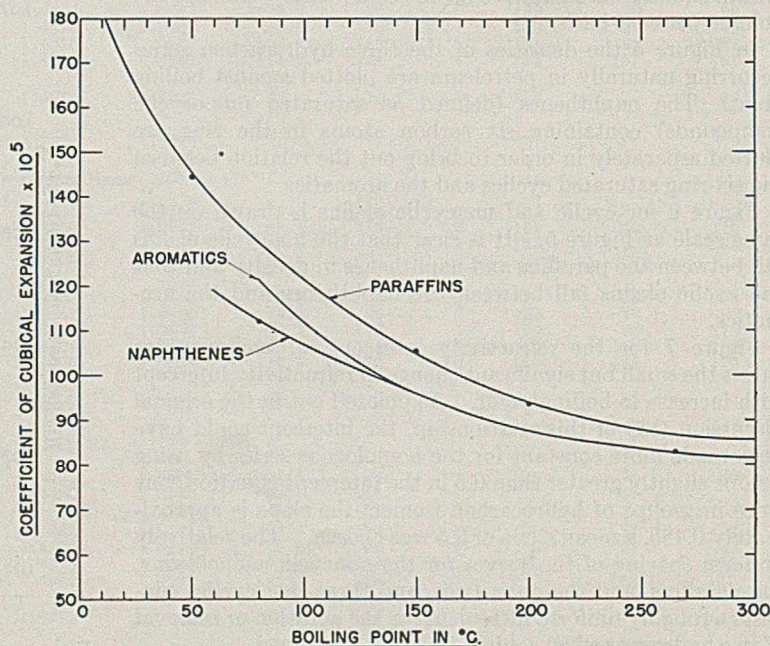


FIGURE 10. COEFFICIENT OF CUBICAL EXPANSION *vs.* BOILING POINT FOR AROMATICS, NAPHTHENES, AND PARAFFINS

TABLE XIV. AVERAGE PROPERTIES OF KNOWN COMPOUNDS IN CUTS OF SPECIFIED BOILING RANGE

Class	No. of Com- pounds	Boiling Point ° C.	Boiling range, 10° to 200° C.)			Derived $F - C$	Dispersion $\times 10^4 (F - C)/d$
			d_4^{20}	n_D^{20}	$n - d/2$		
Noncyclic							
Paraffins	65	121.7	0.7085	1.3998	1.0455	70.4	99.0
Monolefins	77	101.8	0.7075	1.4058	1.0521	88.3	124
Nonconjugated diolefins	20	112.1	0.7384	1.4304	1.0612	104.3	143
Conjugated diolefins	31	111.7	0.7430	1.4524	1.0809	156.6	211
Monocyclic							
Naphthenes (all)	80	133.1	0.7772	1.4281	1.0395	76.9	99
Naphthenes (C ₆ ring only)	46	152.0	0.7942	1.4376	1.0405	78.6	99
Monolefins	66	135.3	0.8087	1.4496	1.0453	95.5	118
Conjugated diolefins	10	121.0	0.8353	1.4772	1.0596	154	185
Aromatics	43	176.6	0.8682	1.4968	1.0627	148	171
Dicyclic							
Saturated	19	159	0.8501	1.4576	1.0326	84.1	99.0
Tricyclic							
Saturated	2	164.5	0.8725	1.4604	1.0242	86.3	99

properties of the different hydrocarbon series in comparison to each other. This is particularly true of the refractivity intercepts, dispersions, and specific dispersions.

Effect of Temperature and Pressure on Density and Refractive Index

Various methods of generalizing the change of density for ° C. for different types of compounds were tried. The method of Beale (19), in which cubical coefficient of expansion is plotted against boiling point, has the merit that the curves for the paraffins and the aromatics are approximately parallel. This lends strength to the idea that this method of plotting is fundamentally sound.

Figure 10 for the cubical coefficient of expansion *vs.* boiling point is almost identical with that of Beale (19) as far as paraffins and aromatics are concerned. Data for 22 naphthenes were plotted on this type of graph. The data for the higher boiling naphthenes were erratic and scattered on both sides of the curve for the aromatics. It was therefore decided not to attempt at this time to draw separate curves for the higher boiling aromatics and naphthenes. Data for 32 cyclic unsaturated compounds showed similar scattering around the aromatic-naphthene curve; therefore, it is recommended that the naphthene curve be used for these compounds also. Similarly, in the case of the noncyclic olefins and diolefins, there is at present an insufficient amount of reliable data to justify a curve distinct from that for the paraffins. Accordingly, the paraffin curve is recommended for all noncyclic hydrocarbons.

The cubical coefficient of expansion is useful, since when multiplied by the density it yields the increment of density change per degree change in tempera-

Figure 11 is derived by multiplying the cubical coefficient of expansion obtained from Figure 10 by the densities read from Figures 5 and 6. In addition, the density change data from the unabridged petroleum tables (107) have been plotted. It is significant that as density increases in each homologous series, other than the aromatics, the curve for each series tends to bend towards the curve for petroleum. The accentuated divergence between the curves for the saturated cyclic with six-membered rings and all saturated cyclic is also of interest.

Figure 12 has been prepared as an aid in correcting from specific gravity at 60° F., which is the usual standard in the petroleum industry, to d_4^{20} which is needed for calculating the refractivity intercept or specific dispersion at 20° C. This curve involves the coefficient of expansion based on the unabridged National Standard Petroleum

Tables and the change in density of water between 60° F. (15.56° C.) and 40° C.

Figures 11 and 12 are, of course, intended primarily as a practical aid in correcting densities to 20° C. when they are found in the literature at other temperatures. The corresponding refractive index correction will be given with reasonable accuracy by the equation

$$\Delta n = 0.60 \Delta d \quad (3)$$

This equation is based both on the Eykman equation and on empirical observation (88, 156). In case refractive index data are to be corrected over a wide range for the effect of either pressure or temperature, the Eykman equation can be used with confidence provided the change in density is known (57, 88, pp. 697-704). It is also possible, as shown by Kurtz and Ward (88, p. 723) to express the relationship between refractive index and density by means of an equation of the Sellmeier-Drude type in which a coefficient for the effect of tem-

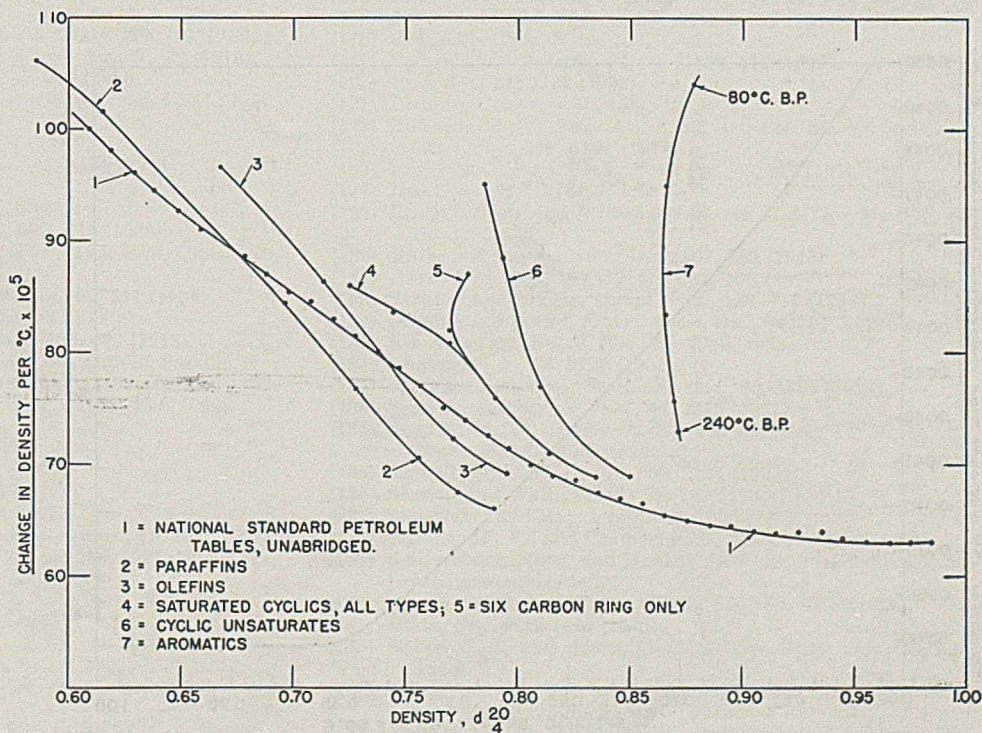


FIGURE 11. CHANGE IN DENSITY PER DEGREE CHANGE IN TEMPERATURE *vs.* DENSITY FOR FIVE HYDROCARBON SERIES AND FOR PETROLEUM

perature or pressure on the frequency of vibration of the dispersion electrons is introduced. The coefficient of frequency change is fortunately proportional to the density change; therefore, if the change in density with temperature or pressure is known, the change in refractive index can be calculated. For example, the excellent data of Gibson and Kincaid (57) for the effect of pressure and temperature on benzene are, as shown by Table XV, accurately represented by the equation

$$n^2 - 1 = \frac{B}{(V_0 + \phi)^2 - V^2} \quad (4)$$

where n = the refractive index
 B = a constant characteristic of each compound = $\frac{\text{dispersion electrons per gram} \times \text{density}}{1.2403 \times 10^{-8}} = 6.0886 \times 10^{30} \times \text{density}$
 V_0 = characteristic frequency of dispersion electrons in benzene = 2.1288×10^{15}
 V = frequency of light used; $V^2 = 0.47344 \times 10^{30}$ for hydrogen line at $436 \text{ m}\mu$; $V^2 = 0.25892 \times 10^{30}$ for average sodium line at $589 \text{ m}\mu$
 ϕ = increment of frequency of dispersion electrons due to effect of temperature or pressure = $(0.87366 - \text{density}) 3.14 \times 10^{14}$

This equation was obtained by interpolation, using the Eykman equation to obtain refractive indices for the 589 and 436 lines at the same pressure, then solving for B and V_0 . The number of electrons per gram was found to be reasonably constant, the average value being 7.5517×10^{22} . As previously shown, $B = \frac{\text{density} \times \text{electrons per gram}}{1.2403 \times 10^{-8}}$. Therefore in this case, $B = \text{density} \times 6.0886 \times 10^{30}$. From the point of view of ease of use, the Eykman equation is in some respects more simple than Equation 4. From a theoretical point of view, it is very significant that the effect of temperature or pressure on the relationship between density and refractive index can be accurately represented by an equation in the Sellmeier-Drude form, provided the frequency of vibration is corrected for the

TABLE XV. CALCULATION OF REFRACTIVE INDEX OF BENZENE FROM DENSITY AT VARIOUS TEMPERATURES AND PRESSURES

(Using the modified Sellmeier-Drude equation containing a coefficient for the change in frequency at vibration of the dispersion electrons, using data of Gibson and Kincaid)

Wave Length $\text{m}\mu$	Temperature $^{\circ}\text{C}$.	Pressure in Bars	Density	Calcd. n	Obsd. n	$\Delta n \times 10^4$
589	25	1	0.87366	1.4983	1.4983	0
		272	0.89430	1.5108	1.5108	0
		617	0.91580	1.5239	1.5240	-1
		868	0.92927	1.5322	1.5323	-1
	45	1	0.85220	1.4853	1.4851	+2
		547	0.89460	1.5110	1.5108	+2
		919	0.91618	1.5242	1.5242	0
		1188	0.92959	1.5324	1.5324	0
436	25	1	0.87366	1.5201	1.5201	0
		26	0.87576	1.5214	1.5212	+2
		343	0.89911	1.5363	1.5365	-2
		561	0.91264	1.5450	1.5449	+1
	45	1	0.8522	1.5065	1.5065	0
		280	0.8760	1.5215	1.5214	+1
		629	0.8997	1.5367	1.5366	+1
		867	0.9134	1.5455	1.5450	+5

influence of temperature or pressure in accordance with Equation 4 of this paper or Equation 66 of a previous paper (88).

It will be observed that in 16 calculations, the difference between the calculated and observed refractive index was greater than 0.0002 in only one instance.

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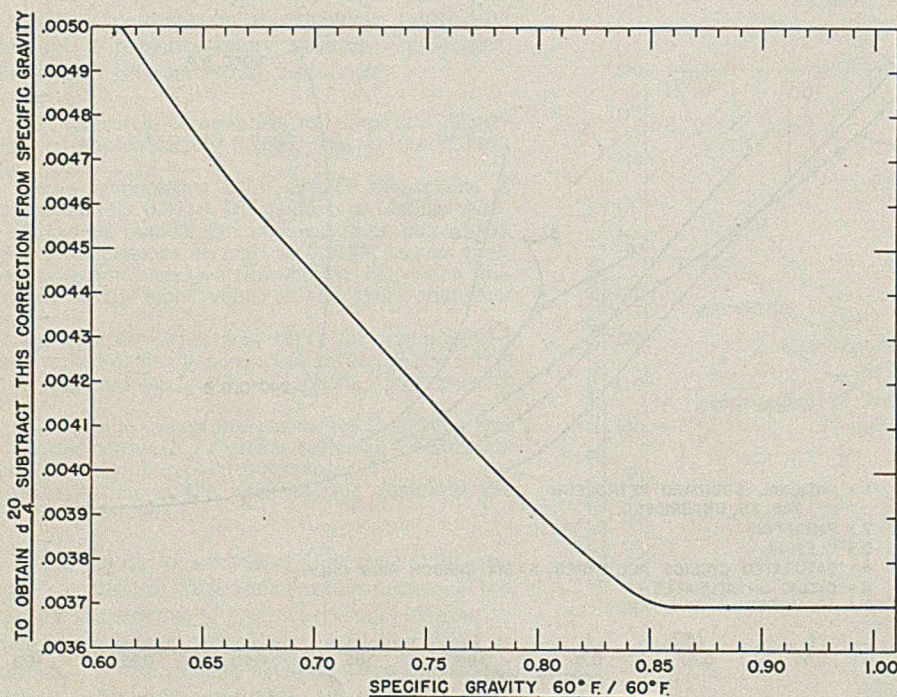


FIGURE 12. CONVERSION FROM SPECIFIC GRAVITY 60/60° F. TO DENSITY 20/4 FOR PETROLEUM

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Determination of Mercury with s-Diphenylcarbazine

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THE reaction of mercuric ions with s-diphenylcarbazine to yield a purple aqueous solution is recognized as a very sensitive reaction, given by one part of mercury in 100,000 parts of water (1, 5). The methods of obtaining the mercury from the sample and the preparation of the aqueous solution have been carefully studied (6, 8, 9). This reaction is influenced by many factors, such as the pH of the solution, exposure to air, ratio of reagent to metal, etc., but no systematic investigation of these influences has been reported in the literature. The purpose of the present paper is to describe a study of the conditions necessary for the accurate determination of mercury with diphenylcarbazine.

Apparatus and Methods

The color determinations were made with a photoelectric colorimeter (a description of which is soon to be published), designed by C. W. Fleetwood of this laboratory. It uses as its light-measuring elements two Weston photonic cells, which are electrically opposed, and the current developed by them is balanced by means of a variable resistance. When a colored solution is interposed between one cell and the source of light, this variable resistance, R_1 , is adjusted until balance is again restored. The light absorption of the solution is thus measured in terms of the ohms required to secure the balance. A sensitive galvanometer serves as the indicating instrument. All measurements were made in 10-cm. cells.

All pH measurements were made with a glass electrode, in the circuit of which was inserted a vacuum-tube apparatus operating at the open grid potential.

Standard solutions of mercury were prepared by dissolving weighed amounts of Mallinckrodt's analytical reagent quality mercuric chloride, mercuric nitrate, and mercuric sulfate, respectively, in triple-distilled water. The s-diphenylcarbazine was obtained from the Eastman Kodak Company and showed a melting point of 172-173°. All weights, pipets, burets, and volumetric flasks were calibrated by standard methods.

The Reagent

Absolute alcohol was found to be the most satisfactory solvent for the diphenylcarbazine and a 1 per cent (approximately saturated) solution the most desirable concentration. The minimum amount of alcohol was necessary because the rate of color destruction of the mercury solutions is proportional to the alcoholic content. Since the reagent solution was found to discolor upon standing for 24 hours, it was always prepared during the day on which it was used. It was preserved in a glass-stoppered bottle and stored in a dark place, since light and atmospheric oxygen hastened the discoloration.

The Color Reaction

The curve in Figure 1 shows the extent to which the color is dependent on the mercury concentration over the range studied. The intensity of the color developed upon the addition of the diphenylcarbazine was found to be independent of the amount of the latter, provided the ratio of the reagent to the mercury was 2 to 1 or greater. This ratio might serve as evidence that the colored product is Feigl and Lederer's (2) inner metal complex (a carbazine) with the formula Hg_2Dc and not a carbazone as suggested by Cazeneuve (1), Stock and Zimmermann (8), and others.

Rate of Color Formation

In all the work with the mercury solutions, the maximum color intensity was attained within 15 minutes after the addition of the diphenylcarbazine. The order of mixing the reagent and mercury solution, the amount of stirring, and the concentration of the metal had no effect on the rate of color formation. However, the procedure followed was to pipet the reagent drop by drop into the Erlenmeyer flask containing

the mercury solution, shaking the flask after the addition of each drop. No fading of the color solution occurred within a period of several hours, provided the solutions were not unduly exposed to atmospheric oxygen.

Influence of Various Ions

Stock and Pohland (7) report that the mercury determination cannot be made in the presence of zinc, iron, cobalt, nickel, lead, copper, silver, gold, cyanides, bromides, or iodides (these latter three can be present in minute quantities). These same authors find that sodium, potassium, ammonium, magnesium, calcium, strontium, barium, aluminum, manganese, fluorides, and chlorides (provided the concentration of the latter two is not large) are without influence upon the determination. Obviously, chromate ions must be absent, since even in strongly acid solutions they give an intense violet color with diphenylcarbazide (1).

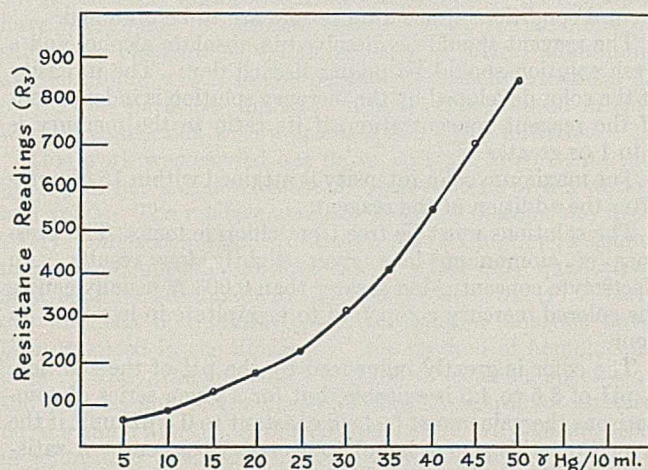


FIGURE 1. RELATION OF COLOR INTENSITY TO MERCURY CONCENTRATION

Preliminary work verified the above findings with some exceptions. Zinc did not interfere until the concentration was five times that of the mercury. Cadmium was found to belong to the noninterference list and chlorides were found to have a very destructive action upon the colored mercury compound. In view of the fact that free chlorine is frequently used in getting mercury into solution (6, 8, 9), a quantitative study of the influence of chloride ions was made.

The results showed that the chloride ion, whether the anion of a metal or the acid, caused, not a flocculation of the colored compound but a decomposition into colorless soluble products. A chloride-ion concentration greater than 0.0001 *N* (3.5 mg. per liter) produced the color destruction.

Majer's (4) conclusion that ammonium ions also have a destructive effect on the colored mercury compound was verified. However, he attributed a much greater effect to the ammonium ion than the authors' experiments would justify. This lack of agreement is probably due to the fact that Majer studied the effect of ammonium chloride instead of an ammonium salt in which the anion had no influence. The presence of ammonium ions up to a concentration sufficient to cause precipitation gave readings only slightly lower than solutions of like mercury contents without ammonium ions, and the destructive effect produced by ammonium chloride was only slightly greater than that caused by an equivalent amount of sodium chloride.

All work with the influence of the various ions indicated

that the greater the electrolyte concentration the greater the precipitation tendency of the colored mercury compound. The nitrates and sulfates of potassium, sodium, and ammonium were chosen as typical salts and the influence of various concentrations on the precipitation time was noted. The presence of these salts was found to be without influence until the concentration reached 0.003 *N* to 0.004 *N* (200 to 400 mg. per liter depending upon the molecular weight) when precipitation took place in less than an hour. Precipitation usually occurred sooner in solutions containing ammonium salts than in those containing an equivalent amount of the corresponding sodium or potassium salt.

Flocculation studies made with solutions of pH values ranging from 3.5 to 6.3 showed that the higher the pH the greater the tendency to precipitation. In fact, at a pH above 6, a precipitate frequently appeared in a short time without the presence of an electrolyte. Another feature noted was that the higher the concentration of mercury, the smaller the concentration of electrolyte needed to cause flocculation of the colored mercury compound.

Hydrogen-Ion Concentration

Above a pH of 7 the diphenylcarbazide functions as a hydrogen-ion indicator, the colorless solution taking on an orange hue. The hydrogen-ion concentration also has a decided influence on the reaction between mercuric ions and diphenylcarbazide. Stock and Zimmermann (8) reported that the reaction is best carried out in a neutral solution and suggested the use of either urea or sodium acetate (the choice depending upon the concentration of mercury) to adjust the pH. Thilenius and Winzer (9) gave a pH of 3 to 4 as the maximum stability value, but apparently did not differentiate between the influence of the hydrogen ion and that of the chloride ion. In this work a more extensive study of the effect of the hydrogen-ion concentration was made and the optimum pH range for the color reaction was determined. The experiments showed that the color could exist with varying intensities over a fairly wide pH range (approximately 2.6 to 7); below 2.6 the solution was decolorized and above 7 the color effect of the reagent interfered. It was evident, therefore, that if solutions are to be compared accurately, the pH values must either be similar or in a range where there is little variation of color intensity with pH. Attempts to buffer the mercury solutions with urea were unsuccessful; the addition of urea did not satisfactorily adjust the pH and greatly increased the flocculation tendency of the mercury diphenylcarbazide.

Attempts to buffer the solution by the addition of a saturated sodium acetate solution failed because the pH values of the treated solutions frequently differed so much that solutions of like mercury concentrations gave unlike readings.

A study was made to find the pH range in which the color intensity of mercury solutions of the same concentration showed the smallest variation. This was found to be from 3.5 to 4.5. Therefore, a pH value of 4 was considered the optimum for mercury determinations with diphenylcarbazide. However, although the shift in color is less pronounced between pH 3.5 and 4.5, even between these limits it is great enough to require holding the pH constant within ± 0.3 unit for accurate determinations.

It was found that a satisfactory adjustment of pH values could be accomplished with a precision of ± 0.1 pH unit by titrating with dilute acetic acid or sodium acetate, using the glass electrode as an indicator. The precision with bromophenol blue as the indicator was slightly less, but still sufficient for accurate determinations. These titrations with a colored indicator were performed on an aliquot portion, not on the solution to which the diphenylcarbazide was added.

The addition of either acetic acid or sodium acetate did not interfere with the color reaction, provided that the total electrolyte concentration did not exceed the salting out value and cause the precipitation of the colored complex.

The use of potassium acid phthalate as a buffer was abandoned, since precise results were not obtained with it.

Lambert-Beer Law

According to the Lambert-Beer law and the electrical setup of the colorimeter, the molecular concentration of mercury, c , should be a linear function of $\log(1 + \frac{R_3}{R_2})$, where R_2 represents the fixed resistance and R_3 the number of ohms necessary to restore balance when the colored solution is placed between the source of light and photonic cell. As is shown in Figure 2, the colored mercury solutions did not con-

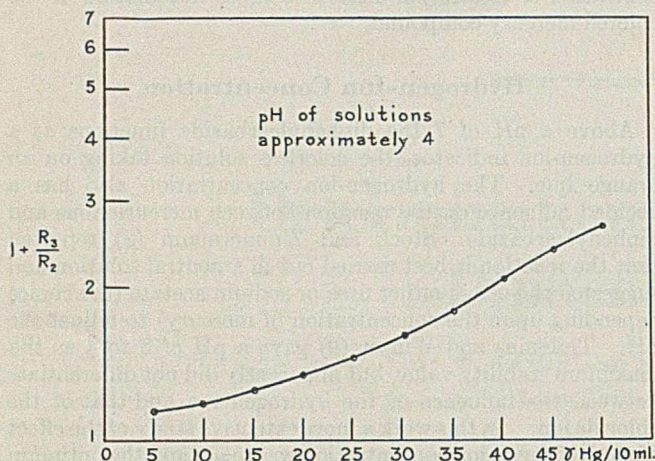


FIGURE 2. CONFORMITY OF COLORED SOLUTIONS TO THE LAMBERT-BEER LAW

form to this linear relationship predicted by the Lambert-Beer law over the total range of concentrations studied (5 to 50 γ of mercury per 10 ml.). However, an examination of Figure 2 shows that the law is followed within the experimental error over somewhat smaller ranges of concentration.

Sensitivity

The sensitivity data for mercury solutions of pH values of approximately 4 are given in Table I.

The number of milligrams of mercury producing a perceptible difference in 20 ml. of solution is designated by Δ and listed in the third column. In the first column are listed the volumes in liters containing one gram atom of mercury. Column B represents the total number of milligrams of mercury in 20 ml. of solution. The sensitivity, S , is the reciprocal of the figure recorded in column 3. $B' = B + \Delta$.

The values of S indicate that the sensitivity is approximately the same at the different concentrations until a concentration of 0.09 mg. per 20 ml. is reached, when the sensitivity decreases. There is also a smaller decrease in sensitivity at a concentration of 0.03 mg. per 20 ml.

Horn (9) has suggested that the ratio B/B' is probably constant throughout colorimetry, independent of the color examined. He found this true in the case of CrO_4^{--} , Cu^{++} , and $\text{Cu}(\text{NH}_3)_4^{++}$, respectively. Yoe and Hill (11), Yoe and Wirsing (12), and Yoe and Hall (10) have extended this investigation to other colored solutions and have likewise found that the B/B' ratio is approximately a constant, with a value

around 0.90 to 0.95. The values obtained in this work for mercury are slightly higher than previously determined B/B' ratios, although one is hardly justified in making this comparison since the values of previous experimenters were obtained by visual observations.

TABLE I. SENSITIVITIES AT VARIOUS MERCURY CONCENTRATIONS

V	B	Δ	S	B'	B/B'
401,220	0.01	0.00074	1,350	0.01074	0.930
133,726	0.03	0.00085	1,176	0.03085	0.972
80,244	0.05	0.00074	1,350	0.05074	0.985
57,173	0.07	0.00072	1,398	0.07072	0.989
44,576	0.09	0.00096	1,041	0.09096	0.989

Summary

The colorimetric method of determining mercury with diphenylcarbazide necessitates a careful control of experimental conditions if accurate results are to be obtained.

The reagent should be dissolved in absolute alcohol and a fresh solution should be prepared each day. The intensity of the color developed by the mercury solution is independent of the reagent concentration, if its ratio to the mercury is 2 to 1 or greater.

The maximum color intensity is attained within 15 minutes after the addition of the reagent.

The solutions must be free from chloride ions. The presence of ammonium ions gives slightly low results. An electrolyte concentration greater than 0.003 N usually causes the colored mercury compound to precipitate in less than an hour.

The color is greatly influenced by the pH of the solution. A pH of 3.5 to 4.5 is suitable, but for a given series of comparisons the value must be held constant to 0.3 pH unit if the error from this source is not to exceed 5 per cent. A satisfactory pH may be secured by titration on an aliquot of the sample solution with dilute acetic acid or sodium acetate, using either the glass electrode or bromophenol blue as the indicator.

If the foregoing experimental conditions are observed, and the thickness of the solution layer is 10 cm., diphenylcarbazide will determine quantitatively as little as 0.4 mg. of mercury in a liter of solution with a precision of approximately 5 per cent. For quantities ranging from 5 to 50 γ per 10 ml. the average precision is about 3 per cent. When a colorimeter of the Duboseq type with setting at 20 was used for the observations, the sensitivity was decreased. Precise determinations could not be made on solutions containing less than 0.8 mg. of mercury per liter. No attempt was made to increase the sensitivity in either method by using color filters.

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Quantitative Spectrographic Estimation of Trace Elements in Biological Ash

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PROBLEMS dealing with mineral content of foods are of interest not only because of their biological bearing but also because of the general type of analytical methods which must be employed. Very accurate gravimetric and volumetric analyses have been developed for the elements present in large quantities, such as sulfur, phosphorus, sodium, potassium, magnesium, and calcium. However, for most other elements these methods require a larger amount of material than is available from samples of reasonable size. Where only small samples are available, spectrographic methods have been used for the analysis of the elements present in relatively high concentrations (2, 3), but no attempts have been made to estimate quantitatively the amounts of such trace elements as vanadium, copper, silver, aluminum, and titanium, which might be present in concentrations of only a few parts per million. Interest was aroused in this work in connection with a problem in poultry nutrition.

This work was carried out in an attempt to correlate the quality of hen's eggs with the mineral content of the whites and yolks. The relative analyses of highly viscous and relatively nonviscous eggs are known for sodium, potassium, magnesium, phosphorus, and calcium, but only qualitative analyses have been made for the "trace" elements (1). Various methods of quantitative spectrographic analysis have been reported in the literature: the method of homologous lines (4, 7, 8), the customary method of exposing spectra of the samples and of the corresponding standards alternately on the same film (6), and an internal standard element used in connection with light-intensity measurements (2).

In order to facilitate the analysis of a large number of samples the method of standard curves was employed (3). While this method does not give the ultimate in precision, it lends itself to the quantitative estimation of metallic content of many types of samples where several elements are present, and gives reproducible results.

Apparatus and Technic

A Central Scientific Company replica, 20,000 lines per 2.5-cm. (1-inch) grating with a focal length of 106 cm., was used in this investigation. The dispersion of the instrument was 8.7 Å. per mm. at 2500 Å. and 10.0 Å. per mm. at 4000 Å. The method of excitation of the sample was that described previously (3, 6). Graphite rods of the best spectrographic grade obtainable from Bausch & Lomb Optical Company were used. They were 7.8 mm. (0.3 inch) in diameter and about 5 cm. (2 inches) in length. The lower electrode, which served as anode, contained a well for the sample 9.4 mm. (0.375 inch) in depth and 4.7 mm. (0.19 inch) in diameter. Both electrodes were mounted vertically.

Two hundred and twenty volts direct current were used with a heavy ballast resistance. The current was maintained at 9 amperes during exposures by adjustment of the gap distance. The graphite electrodes were refluxed in concentrated nitric acid vapors for 4 days to eliminate traces of iron and vanadium which were found to be present after drilling the well, and were then refluxed in triple-distilled water and dried at 110° C. Since only very small amounts of the ash were available for analysis, the samples were treated in the following manner:

The concentration used was 0.00676 gram per cc. This particular value was used only because the amount of the smallest sample was such as to make this concentration convenient in the glassware available. The dry ash was weighed directly in small calibrated flasks, pure concentrated nitric acid was added, and the solutions were digested for 8 hours at 100° C. and finally made up to volume. No base material was added, as has been recommended (3), since it was shown that the large quantities of sodium, potassium, magnesium, calcium, and phosphorus present

were sufficient to cause the arc to run smoothly. The previously treated graphite electrodes were arced for 1 minute to drive off any traces of impurities and to increase the porosity. After cooling, 0.6 cc. of the sample solution was added by repeated additions and drying. This method of successive additions was necessary in order to put enough sample in the anode electrode. Using this amount of solution, 4.06 grams of ash were deposited in the anode. After the addition of the solution the electrodes were finally dried for 1 hour at 110° C.

Eastman Commercial film was used in all work. This film recorded wave lengths down to 2400 Å. and was amply sensitive in the region used (2500 to 3400 Å.). The slit width employed was 0.009 cm. in all cases. The electrodes were preadjusted and the shutter was kept open, so that the exposure began as soon as the arc was started. Each exposure was made for exactly 1 minute from the time of striking the arc. It has been shown previously (3) that samples of this type and size are completely volatilized within 1 minute. Trials showed that, for the samples used in this investigation, this was indeed the case. The films were developed for 4 minutes at 20° C. in Eastman developer formula D72, using a fresh portion of developer for each film to ensure uniform development.

The density of the lines was measured with a simplified microdensitometer. A General Electric light-sensitive cell was connected in series with a Leeds & Northrup type R galvanometer, using a scale with radius of 1 meter. Illumination was furnished by a Westinghouse type H-3, 85-watt, high-intensity mercury vapor lamp. The linear source of light from this lamp was focused on the film by a lens to give an intensely illuminated strip, shorter than the line to be measured and nearly as narrow. The film was clamped to a horizontal carriage which was connected to a fine screw adjustment, by which the film might be moved accurately as small a distance as 0.0005 cm. (0.0002 inch). Directly below the film a defining slit, slightly narrower than the spectral lines, was placed to cut out extraneous light rays. The light-sensitive cell was placed approximately 3 cm. below this defining slit, enclosed in a light-tight box with the slit the only opening. The principal advantage of this arrangement lies in the high intensity of light passing through the line.

The blackness of each line was measured by obtaining the minimum deflection of the galvanometer and subtracting from the background reading (9). The background readings were fairly uniform, so that these values represent the line blackness with sufficient accuracy for the purpose at hand.

Analysis of Films

A qualitative analysis of the films, using an iron comparison spectrum, showed calcium, magnesium, potassium, sodium, and phosphorus all present in large quantities; aluminum, boron, copper, iron, manganese, silicon, silver, titanium, and vanadium present in smaller quantities. None of the persistent lines for the other elements was detected.

Standard solutions for a rough quantitative analysis were made up as follows: A base-line solution was made containing sodium, potassium, calcium, magnesium, and phosphorus in the same proportions as were found in the egg ash by ordinary wet analysis. This solution was made from Baker's analyzed chemicals and contained the five elements used in the ratios: Na, 20.0; K, 19.2; Ca, 1.4; Mg, 1.5; and P, 1.75.

The concentration was adjusted so that the ratio numbers have also the number of grams of element in 100 grams of egg ash. The accuracy of the ratio numbers is shown by the fact that the base-line solution gave lines for these five elements which were almost exactly of the same intensities as the corresponding lines given by egg ash. Any impurities in the Baker's analyzed chemicals gave lines whose measured intensities set down limits on the sensitivity of the final analysis of the egg ash. These lower limits, were, in most cases,

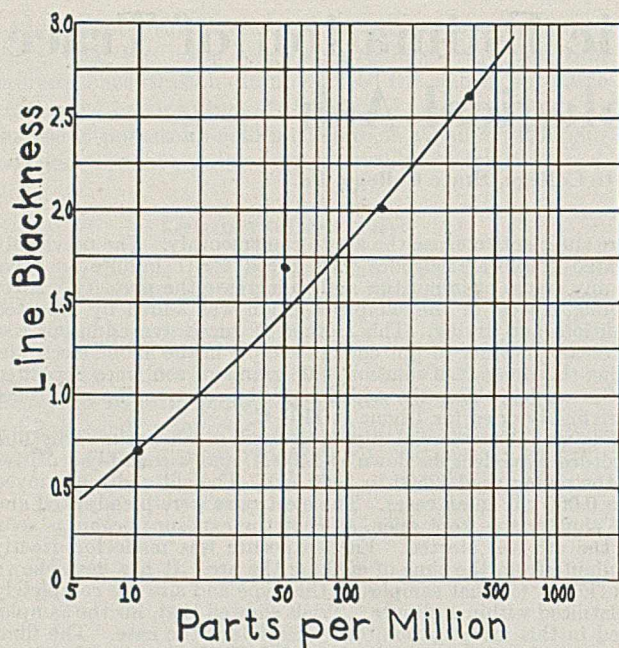


FIGURE 1. STANDARD CURVE FOR SILVER, 3280.67 Å.

sufficiently low for the purpose at hand. A rough quantitative analysis showed that the concentrations of the trace elements in nearly all the egg-ash samples were within the following ranges: iron, less than 100,000 parts per million of dry ash; manganese, vanadium, copper, silver, and titanium, less than 1000 parts per million of dry ash.

Using these results, a series of standard solutions was prepared from the general stock solution, adding the trace elements and concentrating to original volume. These standard solutions had the following concentrations of the trace elements: manganese, vanadium, copper, silver, titanium, and aluminum, 10, 20, 50, 150, 400, and 1000 p. p. m. on basis of dry ash; iron, 50, 150, 500, 1500, 5000, 10,000, 30,000, and 60,000 p. p. m. on basis of dry ash.

Spectra were made of these standards using conditions identical with those used for the egg-ash samples. Observation of the standard spectra indicated that the following lines were the most sensitive over the ranges of concentration being used: manganese, 2576.12 Å.; iron, unresolved doublet 3020.65 to 3021.08 Å.; vanadium, 3185.406 Å.; copper, 3273.97 Å.; silver, 3280.67 Å.; and titanium, 3349.04 Å.

The blackness of these lines was measured with the microdensitometer and expressed in arbitrary units from the scale of the galvanometer. These values were plotted as ordinates against parts per million of the element, using semilogarithmic paper. Only the most persistent line of aluminum, at 3961.54 Å., could be positively identified. However, it showed no gradation of intensity with decreasing concentration and could be used only in a qualitative way. The line of manganese at 2576.17 Å. is not sensitive below 50 p. p. m. but had to be used, since the most persistent line 4030.76 Å. appeared in the cyanogen bands and was therefore not suitable for analysis. Analysis was not made for boron and silicon, although their persistent lines were observed in the sample spectra. The spectra of the purified carbons

themselves gave these lines in varying concentrations; hence it was impossible to make analyses for these elements using graphite electrodes. Rough quantitative analyses were then made for the six elements by comparing the standard curves of Figures 1, 2, 3, and 4 with the blackness of the corresponding spectral lines from egg ash.

TABLE I. ANALYSES OF ASH OF EGG WHITES

Elements	Average of 10 Firm Whites P. p. m.	Average of 7 Watery Whites P. p. m.
Manganese	< 50	< 50
Iron	53	81
Vanadium	240	650
Copper	137	600
Silver	52	25
Titanium	84	850
Silicon	+	+
Aluminum	++	++
Phosphorus	+ or ++	+

It was shown by making repeated spectra from the same sample solution that the line-blackness measurements could be repeated with the following precision: silver, vanadium, titanium, and manganese to 0.1 division as shown on the graphs. Results could be duplicated to 0.2 division for iron.

Results

Rough quantitative analyses for manganese, iron, vanadium, copper, silver, and titanium were made of the ash of separate whites and yolks of high- and low-viscosity eggs, and estimates were made as to the relative amounts of silicon, aluminum, and phosphorus. No difficulty was found in duplicating, within 15 per cent, successive analyses from a given sample. However, the analyses of supposedly similar successive samples varied many fold. Only average values for several apparently similar successive samples are given in Tables I to V.

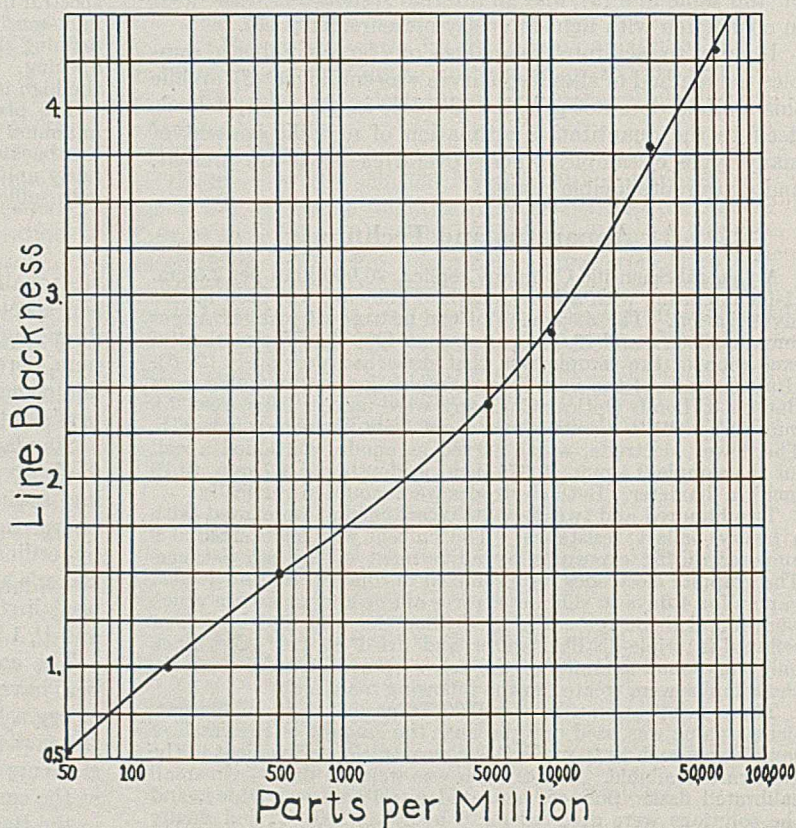


FIGURE 2. STANDARD CURVE FOR IRON
Unresolved doublet, 3020.65 to 3021.08 Å.

The symbols used in these tables to indicate the approximate amounts of these elements, estimated on the basis of spectra of standard solutions, are as follows:

Aluminum, + = 0 to 100 p. p. m.; ++ = 100 to 500 p. p. m.; +++ = 500 to 1000 p. p. m.
 Phosphorus, + = 0 to 1000 p. p. m.; ++ = 1000 to 5000 p. p. m.; +++ = 5000 to 20,000 p. p. m.

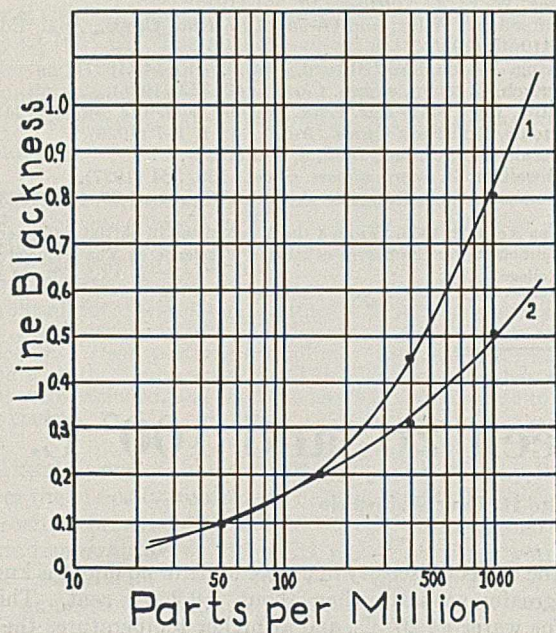


FIGURE 3. STANDARD CURVES

1. Manganese, 2576.12 Å.
2. Vanadium, 3185.406 Å.

Since silicon was present in the graphite electrodes used, no standards were made up with it present. Hence, it was impossible to give any estimate of amount present. However, the amounts of silicon present in the purified electrodes were in nearly every case much less than in any of the samples tested.

The egg whites analyzed were total whites and no separations were made of the white into its different divisions.

In addition to the analyses given in Tables I and II, analyses were made of the mineral content of the ash of the feed, and of the blood, liver, oviduct, and eggs from hens producing viscous and nonviscous eggs.

TABLE II. ANALYSES OF ASH OF EGG YOLKS

Elements	Average of	Average of
	2 Poor Yolks	6 Good Yolks
	P. p. m.	P. p. m.
Manganese	< 50	50
Iron	2500	3000
Vanadium	200	200
Copper	130	200
Silver	2	4
Titanium	600	450
Silicon	+	+
Aluminum	+++	+++
Phosphorus	+++	+++

Other work was carried out trying to trace the presence of certain elements which were found in the feed ration through the egg and finally to the chick. The feeds used in these experiments had 40 parts per million of manganese added as manganese carbonate. The ash analyzed was approximately 10 per cent of the weight of the feed, hence 400 p. p. m. could be attributed to the addition of manganese car-

TABLE III. ANALYSES OF ASH OF EGGS AND ORGANS OF HENS LAYING VISCIOUS EGGS AND OF THEIR FEED

Element	Feed	Blood	Liver	Oviduct	Egg Whites	Egg Yolks
	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
Manganese	700	50	< 50	50	50	50
Iron	45,000	100,000	3500	150	50	150
Vanadium	1,400	150	150	150	150	400
Copper	160	160	400	1	250	1
Silver	6	1	1	None	1	1
Titanium	620	220	400	300	1400	400
Silicon	+++	++	+++	None	None	+
Aluminum	+	+	+++	++	++	++
Phosphorus	+++	++++	+++	++	+	++

TABLE IV. ANALYSES OF ASH OF EGGS AND ORGANS OF HENS LAYING NONVISCIOUS EGGS AND OF THEIR FEED

Element	Feed	Blood	Liver	Oviduct	Egg Whites	Egg Yolks
	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
Manganese	700	150	50	50	<50	<50
Iron	45,000	>100,000	>100,000	62	31	5000
Vanadium	1,400	2,000	150	None	150	400
Copper	160	10	800	1	90	250
Silver	6	30	1	1	1	1
Titanium	620	1,000	300	10	1800	1000
Silicon	+++	++	+	None	++	++
Aluminum	+	+	+++	++	++	++
Phosphorus	+++	++	++	++	+	+++

TABLE V. FEEDING PROJECT RESULTS

Elements	Feed 33	Egg 4	Chick 42
	P. p. m.	P. p. m.	P. p. m.
Manganese	6,200	150	<50
Iron	22,000	31,000	40
Vanadium	400	700	50
Copper	10	160	None
Silver	1	10	None
Titanium	400	90	1400
Silicon	++++	+	+
Aluminum	++++	++	+
Phosphorus	++++	++	+

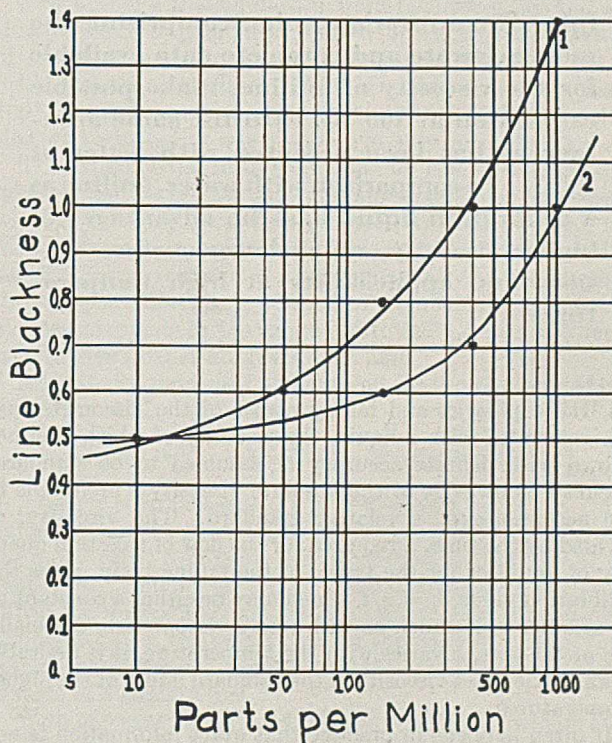


FIGURE 4. STANDARD CURVES

1. Copper, 3273.97 Å.
2. Titanium, 3349.04 Å.

bonate to the feed. Manganese was of special interest, since it has been shown that manganese present in the feed of poultry helps to control perosis (5).

Four such feeding projects were carried out and analyses run on the ash from the feed, egg, and chick. Nothing remarkable was observed from a biological standpoint. A typical analysis is given in Table V.

Analyses were made of still other rations, and also of eggs produced by hens fed these rations. However, no striking results were obtained and these analyses are not tabulated in this article.

Summary

No direct correlation could be made between the quality of eggs and the content of trace elements present in them.

In a qualitative way the amounts of silicon and phosphorus were shown to be greater in the better quality eggs.

The precision of this rapid method of quantitative estimation, made on a relatively inexpensive replica-grating spectrograph, is not greater in extreme cases than 15 per cent.

The author wishes to thank W. J. Rudy of The Pennsylvania State College Poultry Department for the feeding of hens and ashing and preparation of samples; the Central Scientific Company of Chicago, Ill., for the loan of the spectrograph; and Wheeler P. Davey, research professor of physics and chemistry at The Pennsylvania State College, for his counsel and assistance.

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Viscosity of Aniline between 20° and 100° C.

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The viscosity of "chemically pure aniline," $d_4^{20} = 1.0208 \pm 0.0003$, was determined at 5° intervals from 20° to 100° C. with an accuracy of ± 0.20 to ± 0.30 per cent. The measured viscosities were compared with the results in the literature, the latter being in part confirmed and in part found doubtful. The author's results, comprising the most accurate and complete data available for the viscosity of aniline, make possible calibration at 100° C. with the same accuracy as has been accepted with water at 20° C. In comparison with water, aniline as a calibration liquid has the advantages of higher viscosity, much lower surface tension, and applicability at high temperatures.

THE capillaries and falling bodies of the viscometer are calibrated with a liquid, the viscosity of which is either known with definite accuracy or assumed to be standard. Accurate knowledge of the absolute viscosity is preferable to the acceptance of a relative standard. The viscosity, η , divided by the time, t , required for the flow of a certain quantity of liquid or for the travel of the falling body, gives the calibration value, $k = \eta/t$, which may be either a constant or a variable. Inasmuch as with many viscometers, especially the metal ones, k varies with the temperature, it is desirable to know the exact viscosity of the standard liquid at the higher temperatures.

It often happens in practice that exact information is not available regarding the viscosity of a liquid, which otherwise would be suitable for a standard. Naturally the choice of a standard depends upon the accuracy required; at the present

time the correct viscosity in c. g. s. units of no liquid is known with greater accuracy than about ± 0.2 per cent. This is true for water at 20° C., and at higher temperatures the accuracy is far less. Since water has a very low viscosity, it is not suitable for the calibration of apparatus intended for the measurement of high viscosities. Although viscous oils have been measured very accurately, such standards are obtainable only at a high price; moreover, the viscosity of the oils increases about 0.2 to 1 per cent per year, so that they are satisfactory only for a limited time as standards for accurate calibration.

Aniline as Calibration Liquid

Unfortunately, there are no chemically pure stable liquids that have a viscosity approximating that of automobile oil. However, aniline, which is obtainable commercially in pure form at relatively low cost, facilitates the selection of suitable standard liquids. The viscosity of aniline is about four times that of water. Although this difference is not great, one can conveniently measure light oil with a capillary calibrated with aniline, and then utilize this light oil as a standard for measuring the viscosity of viscous oils.

The viscosity curve of aniline was determined in some detail by Bingham, van Klooster, and Kleinspehn (3) in 1919 and by Erk (4) in 1926. The results of other authors were obtained for the most part at room temperature or slightly lower. The viscosity curve is highly important, because, as already pointed out, the constants of many viscometers change with the temperature. The determination of the viscometer constant at room temperature and at only one viscosity is insufficient for many practical problems and entirely untrustworthy for scientific purposes.

Viscosity Measurements

With the aid of a Steiner falling-body viscometer, Type MLD, the author, using two bodies, measured the dynamic viscosity (centipoises) of aniline at 20° C. Commercial chemically pure aniline, which had a very slight yellow

color, was vacuum-distilled for use, although the viscosity was not altered by the distillation. As measured with a pycnometer its density with respect to water at 4° C. was 1.0208 = 0.0003 at 20° C. and 0.9527 = 0.0003 at 100° C. The thermal expansion of the glass was taken into consideration, but the buoyancy of the air was neglected. These figures agree with the results given in the literature. Thus, the published values for 20° C. are given as 1.0203 in Landolt-Börnstein (8), 1.0208 by Erk (5), and 1.0217 in the International Critical Tables (7). The latter give 0.9514 for the density at 100° C. The author's result is less than the I. C. T. value at 20° C. and greater than the I. C. T. value at 100° C., the difference being about 0.001 in each case.

The viscosity at 20° C. was determined under the following conditions:

1. The temperature was read to within $\pm 0.01^\circ \text{C}$.
2. The uncertainty of the corrected thermometer reading amounted to $\pm 0.01^\circ \text{C}$., which corresponds to an uncertainty in the viscosity of ± 0.04 per cent.
3. The time was measured to ± 0.1 second. Measurements were made for a series of temperatures both below and above 20° C., the points were plotted, and the measurements were repeated twice with fresh portions of aniline. Two observers kept the time with three stop watches. Deviations greater than 0.5 per cent were excluded, and the time interval was accurate to ± 0.03 per cent.

The accuracy of the constant, which multiplied by the time gives the viscosity, remains to be estimated. To this end the viscosities between 15° and 18° C. were determined at the same temperatures at which Erk's measurements were made with the fundamental viscometer. The two sets of results are compared in Table I.

TABLE I. COMPARISON OF VISCOSITY MEASUREMENTS BETWEEN 15° AND 18° C.

Temperature ° C.	Viscosity Found by Erk Steiner		Deviation, δ	(100 δ) ²
	Centipoises		%	
15.35	5.20	5.214	0.27	729
16.31	5.01	5.025	0.30	900
16.33	5.02	5.021	0.02	4
16.48	4.93	4.992	1.25	..
16.60	4.97	4.969	0.02	4
17.28	4.85	4.845	0.10	100
17.49	4.84	4.808	0.67	4489
				$\Sigma (100\delta)^2 = 6126$

The data agree very well with the exception of the results at 16.48° C., where the deviation of 1.25 per cent is to be attributed to an error in Erk's result. According to the method of least squares, the probable deviation between the two sets of measurements is $\pm 2/3 [0.6126/(6 \times 5)]^{1/2} = \pm 0.095$ per cent.

The author's results at 20° C. varied between 4.397 and 4.402, and the mean of 6 measurements was 4.400 centipoises. Erk's equation for the viscosity curve of aniline yields a value of 4.36 centipoises at 20° C.; this equation is, however, not reliable. Later in Landolt-Börnstein (9), Erk gave the viscosity as 4.40 centipoises. Bingham, van Klooster, and Kleinspehn found a value of 4.429 centipoises at this temperature, which is 0.66 per cent higher than the author's result. This discrepancy is discussed later.

The possible error in the author's results, comprising uncertainties in the constant k (± 0.10 per cent), the temperature (± 0.04 per cent), and the time (± 0.03 per cent), amounts to ± 0.17 per cent. Considering the uncertainty arising from possible impurities in the aniline, it can be said that the uncertainty in the value 4.400 centipoises is probably ± 0.20 , or at most ± 0.25 per cent.

The foregoing result (4.400 centipoises) for the viscosity of aniline was taken as the standard for the calibration of two

other Steiner viscometers, type MRJ, provided with thermometers whose corrected readings were accurate to $\pm 0.1^\circ \text{C}$. The viscosity of aniline was determined at 5° intervals between 20° and 100° C. with each instrument. The measurement at each temperature comprised five fillings of each viscometer, so that the results (Table II) represent the average of 10 determinations of the time.

TABLE II. VISCOSITY OF ANILINE AT 20° TO 100° C.

Temperature ° C.	Viscosity Found by Steiner	Bingham <i>et al.</i>	Deviation, δ	(100 δ) ²	Accuracy of Steiner's Result \pm %
	Centipoises		%		
20	4.400	4.429	0.66	4356	0.20
25	3.770	3.781	0.29	841	
30	3.218	3.221	0.09	81	
35	2.783	2.826	1.55	Not calcd.	0.30
40	2.432				
45	2.150	2.158	0.37	1369	
50	1.919	0.25
55	1.726	
60	1.557	1.553	0.26	676	
65	1.415	0.20
70	1.296	
75	1.190	
80	1.098	1.094	0.37	1369	0.20
85	1.018	
90	0.9455	
95	0.8817	0.20
98	0.840	0.838	0.24	576	
100	0.8284	
				$\Sigma (100\delta)^2 = 9268$	

Bingham *et al.* determined the viscosity of aniline at certain temperatures up to 100° C. For comparison their results are also given in Table II. With the exception of the result at 35° C. the deviations are relatively small. The next largest deviation is at 20° C. from which it is concluded that the result by Bingham *et al.* for this temperature is high. Using the same procedure in the discussion of Table I for determining the agreement between the sets of data, the method of least squares gives $\pm 2/3 [0.9268/(7 \times 6)]^{1/2} = \pm 0.10$ per cent. This noteworthy result is attributable to the fact that the figure used for time was the average of ten measurements and to the relatively large number of comparison points.

The author's measurements were facilitated by the fact that only 6 cc. of liquid are required for a filling and that a set of measurements for the entire temperature range can be made with the single filling. Liquid used for measurements at 100° C. was always brought to 20° to 40° C. before it was emptied, and a turbidity was observed in only one instance.

The experimental results obtained by Erk in the neighborhood of 80° and 100° C. are apparently very accurate, whereas those at lower temperatures, around 30°, 50°, and 60° C., show wide deviations. This is probably due to Erk's use of different methods of measurement for the two temperature ranges. Since Erk pointed out the lack of precision in his measurements in the range 30° to 60° C., it is not necessary to give further attention to it here.

Erk (6) also published an equation for the viscosity of aniline as a function of temperature:

$$\log (100\eta) = -1.1485 (t - 85.26)/(t + 97.1)$$

in which η is in poises and t is in degrees Centigrade. The values obtained with the aid of this equation are higher than the most recent results for the viscosity of aniline by 0.87 per cent at 20°, 1.60 per cent at 60°, and 0.36 per cent at 100° C. When $\log \eta$ is plotted against the reciprocal of the absolute temperature—a treatment that on the basis of certain theoretical considerations seems profitable—the result is a curved instead of a straight line.

With one exception (Table II) the results of Bingham *et al.* at temperatures above 25° C. and with a single exception (Table I) the results of Erk at room temperatures and in the neighborhood of 80° and 100° C. are, in the author's opinion, accurate figures for the viscosity of aniline. In so far as the

literature available to the author shows, his results are the most accurate and complete data available for temperatures between 20° and 100° C. The average accuracy of the results in Table II is about ± 0.25 centipoise, and the uncertainty of any one result is only as great as is caused by an uncertainty of $\pm 0.1^\circ$ C. in the temperature measurement, which is at least ± 0.20 per cent. The accuracy at 20° C. is obvious from the results in Table I.

There remains the question as to how the results would be affected if aniline was not absolutely pure. The viscosity of a sample of aniline that was darker in color and had a density greater by 0.003 than the product used in the viscosity measurements was observed to be 0.6 per cent higher than that of the purified material. Another sample with the same density as used in the viscosity measurements had the same viscosity. Aniline with a density of 1.014 showed a viscosity of 4.32 centipoises; accordingly, a density change of ± 0.0003 corresponds to a ± 0.07 per cent change in the viscosity. Since an uncertainty of this order is acceptable, the question was not investigated further.

Aniline must be distilled for viscosity measurements, but this is also true of water. When it is protected from light and the atmosphere, aniline can be kept 2 months without change. Aniline vapor attacks paper. The vapor is poisonous only in concentrations higher than those likely to occur incident to viscosity measurements—at least, the author noticed no ill effects. Furthermore, the viscosity of aniline is not especially high. However, in stepwise standardization beginning directly with water, the first step is most uncertain as a consequence of turbulence and surface tension. A viscosity of 4.4 centipoises is sufficiently large to permit convenient standardization of an oil with a viscosity of about 25 centipoises. The latter can then be used for the calibration and control of instruments.

Advantages of Aniline

One great advantage of aniline lies in the fact that its surface tension is only slightly larger than that of lubricating oil. Barr (1) has pointed out the relatively large effect of surface

tension—for example, with capillaries of range 1 of the British Standard BESA-188, an error of 0.8 per cent arises from this cause on changing from water to oil. It is, however, possible to eliminate the influence of surface tension in capillary apparatus. Surface tension had no effect on the author's measurements, because active surfaces are not present in the falling-body apparatus.

Aniline is far more suitable than water for measurements at high temperatures. It can be used in a closed apparatus, such as is provided in the Steiner viscometer, at 100° C. and above without danger of evaporation.

Furthermore, according to Bingham (2), the uncertainty in the present accepted values for the viscosity of water amounts to 0.5 per cent—that is, ± 0.25 per cent. Thus, aniline passes the test in this respect. Whereas water can be employed for calibrations of the required accuracy only at 20° C., distilled aniline having a density of 1.0208 may, with the aid of the results given in this paper, be used for calibration at temperatures from 20° to 100° C. In view of the fact that the constants of many viscometers vary with the temperature, and for other reasons, the ability to calibrate instruments at the higher temperatures appears to be extremely important.

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A Liquid Bath Melting Point Apparatus

THE melting point apparatus represented in Figure 1 combines a high degree of general convenience, moderate rapidity, and a very satisfactory level of accuracy. The design of the outfit and the dimensions indicated are such as to avoid the disadvantages of a large liquid bath, and also difficulties in uniform heat distribution and in heat regulation as the melting point is approached, which may be encountered in the use of very small baths. If strongly made of Pyrex or similar glass, the apparatus is substantial and may be regarded as no more fragile than other glass apparatus. Several outfits of this type have been in use for a number of years, one in the hands of students, without breakage.

The capacity of bulb *A* is about 100 cc. The cap, *H*, seated in a ground joint, has three tubulures, one for the melting point thermometer, *F*, one for the auxiliary thermometer, *G*, and the third for the wiper, *E*. The profile of the apparatus is an unbroken vertical line, with only a convex curvature along the vertical axis. This produces a noticeable horizontal magnification of

objects within the bath, but no distortion. The "bridge," *B*, is attached at two points near the base of the neck and supports the small horizontal platform, *D*. In depressions *a*, *b*, *b* are seated, respectively, the melting point thermometer and the melting point tubes. The support, *D*, and the tubulures mentioned are so placed with respect to each other that the thermometer is parallel with the front wall and about 5 mm. from it, and that the melting point tubes, inserted through the oblique tubulures shown in Figure 1, are seated beside and slightly forward of the bulb of the thermometer, in such position that the rear illumination of the charge in the melting point tube is unimpaired.

When the bath is at room temperature the immersion of the thermometer is about 20 mm. The melting point tubes are about 7 cm. long. The screw-type stirrer, *C*, extends obliquely through opening *O* and between the two supporting arms of *B* to a point near the bottom of the bath and directly beneath platform *D*, and is rotated by a small disk motor with rheostat control. The wiper, *E*, is made from two pipe cleaners joined by twisting two ends together, a free end being then bent into a loop of such diameter that manipulation of the wiper will clear the glass wall of drops or liquid film which decreases the visibility of the thermometer. The apparatus is seated in a 4-cm. circular hole in an

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asbestos board (not shown), and is held in place by means of a clamp attached at *O*. The gas supply is regulated by use of a glass stopcock with an elongated handle.

The melting point thermometer is of the enclosed-scale type, and has the general dimensions of the familiar Anschütz thermometers. It is calibrated for total immersion, with a range from 30° to 300° C. in 1° intervals. The over-all length is 180 mm., the length to the 300° mark is 120 mm., and the diameter is 5 mm. The bulb is 5 mm. high and 5 mm. in diameter at the top, tapering to 3 mm. at the end. The entire scale of the thermometer is within the apparatus. The divisions of the scale are too small to be read satisfactorily with the unaided eye, but by use of the buret reader, *M*, readings to 0.1° can be made with ease. A collar of rubber tubing (not shown), which makes contact with the tubulure of cap *H*, assists in keeping the thermometer in position. A set of short-scale thermometers may be used instead of the single thermometer described.

TABLE I. MELTING POINT DATA

Substance	Melting Point Observed	t^a	N^a	Stem Correction	Calibration Correction	Melting Point Corrected	Accepted Melting Point
Benzoic acid	122.2	76	72	+0.5	-1.1	121.6	...
	122.5	86	72	+0.4	-1.1	121.8	121.7
Benzanilide	163.0	95	113	+1.2	-1.5	162.7	...
	163.2	100	113	+1.1	-1.5	162.8	163
Carbazole	242.2	132	182	+3.3	0.0	245.5	...
	242.4	135	182	3.2	...	245.6	...
	242.4	134	182	3.3	...	245.7	...
	242.7	138	183	3.1	...	245.8	...
	242.0	135	182	3.2	...	245.2	...
					Av.	245.6	244.8

^a Formula used: Correction = $N(t - t^a)0.000154$.

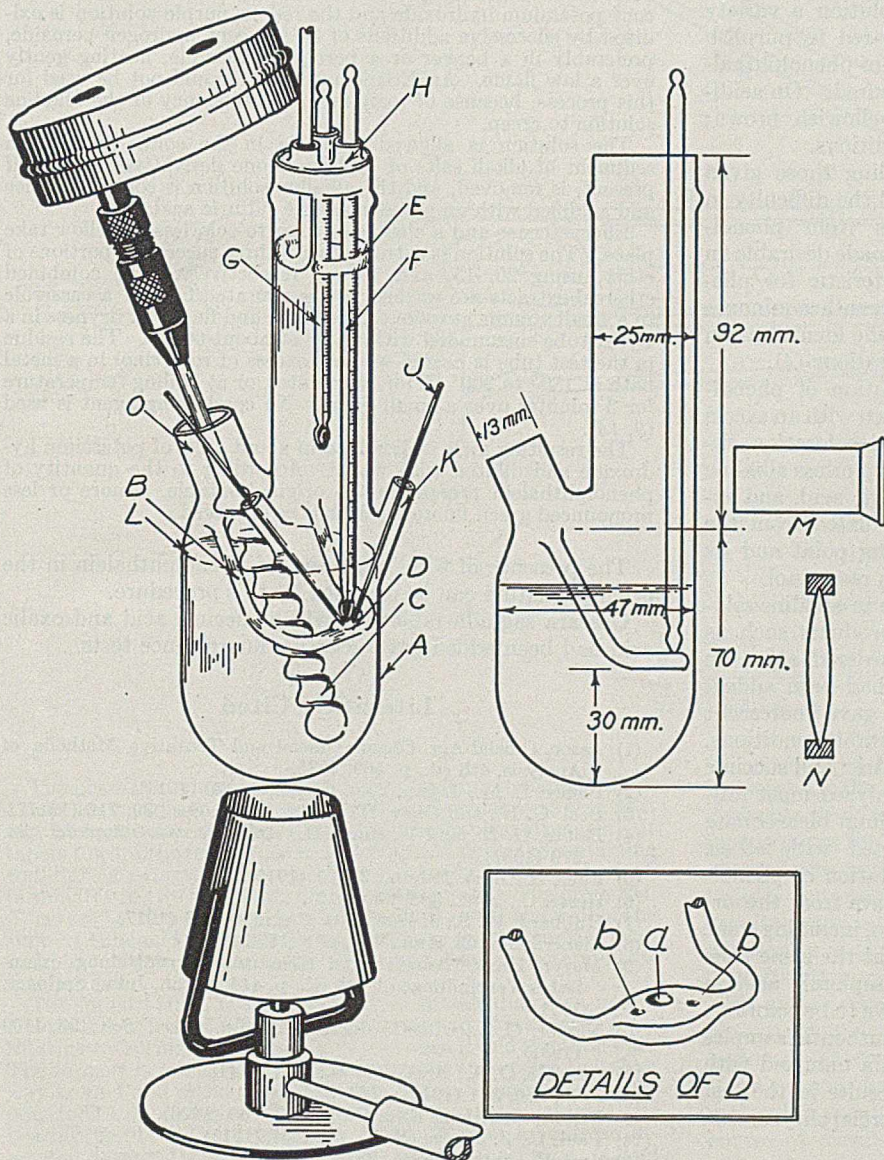


FIGURE 1. MELTING POINT APPARATUS

The auxiliary thermometer, *G*, includes the range 30° to 180° C. on a scale which occupies the lower 55 mm. of the stem—i. e., which is wholly within the apparatus when the thermometer is in the topmost position to which it need be raised in use. This thermometer has a small bulb and is employed in the usual manner for determination of the emergent stem corrections to be applied to the readings of the melting point thermometer. The auxiliary thermometer is held at any desired level by means of a collar of rubber tubing which rests on the tubulure of *H*.

The biconvex lens, *N*, is dispensable, but is desirable as it improves the visibility of the melting point phenomena. The telescope, *M*, and the lens, *N*, are supported by clamps on a small ring stand. A racking device would be an added convenience.

For the trials whose results appear in Table I, thermometer *F* was calibrated by direct comparison with Anschütz thermometers tested by the Bureau of Standards. The melting point tube was in each case introduced when the temperature of the bath was 10° below the melting point of the substance, with the thermometer showing a rise in temperature of 2° per minute. The melting point was taken as the temperature at which a liquid meniscus first appeared. The data recorded in Table I indicate the magnitudes of the stem corrections at several temperatures, the precision of the results, and their accuracy, as determined with several compounds purified by repeated crystallizations.

Detection of Small Amounts of Phenolphthalein

In the Presence of Emodin and of Chrysophanic Acid

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WHEN phenolphthalein is the main active principle in medicinal preparations, its detection and determination are as a rule readily accomplished (1, 18). When, however, it is accompanied by certain laxative plant products, such as cascara, aloes, rhubarb, senna, or frangula, which contain polyhydroxyanthraquinones, its detection may offer considerable difficulties due to the similarity of their chemical behavior (3, 7).

These anthraquinone derivatives—namely, frangula-emodin (also present in cascara sagrada and in rhubarb), aloemodin (also present in senna), and particularly chrysophanic acid (chrysophanol, 2)—show in alkaline solution a variety of rather stable colors (18, 19), from cherry-red to purplish red, sometimes indistinguishable from that of phenolphthalein, the presence of which may thus be obscured. On acidification such solutions turn yellow or yellowish brown; phenolphthalein is colorless under these conditions.

The similarity of color reactions, including those given with concentrated sulfuric acid (11, 16), and the difficulty in separating the anthraquinone derivatives from phenolphthalein by means of organic solvents (19), made desirable an analytical method which would be characteristic for phenolphthalein and negative for the polyhydroxyanthraquinones in question, and thus permit with certainty the identification of phenolphthalein in some medicinal preparations (4).

It was found that the purplish red solution of phenolphthalein in potassium hydroxide when treated with an excess of hydrogen peroxide undergoes a gradual decoloration, resulting from oxidative cleavage. When the colorless alkaline solution is cooled, acidified with dilute sulfuric acid, and extracted with ether, phthalic acid can be isolated from the ethereal extract and identified by its melting point and its ability to yield fluorescein when heated with resorcinol.

When the oxidation by hydrogen peroxide in alkaline solution was carried out upon certain plant products such as rhubarb powder, cascara sagrada, and powdered aloes, to which known amounts of phenolphthalein had been added, oxidation products were obtained which also gave fluorescent solutions on heating with resorcinol under suitable conditions. Since some organic acids like oxalic, malic, citric, and succinic respond in this way, all materials to be analyzed must uniformly first be treated with an excess of sodium bicarbonate solution, and the phenolphthalein extracted with ether. This procedure not only achieves the separation of phenolphthalein and the polyhydroxyanthraquinones from the organic acids and other water-soluble substances, including some anthraglucosides possibly present, but may at the same time reveal the absence of emodin and of chrysophanic acid in samples from which the ethereal extracts prove to be colorless.

Oxidation experiments carried out upon authentic samples of rhubarb, senna, aloes, and cascara sagrada unmixed with phenolphthalein gave uniformly negative results in the test for phthalic acid. Experiments with commercial chrysarobin powder were also negative (5, 6, 17).

The absence of phthalic acid in these oxidation products can well be explained by the following considerations: The anthraquinone derivatives—namely, frangula-emodin, 1,8,6-trihydroxy-3-methylanthraquinone, aloemodin, 1,8-dihydroxy-3-oxymethylanthraquinone, and chrysophanic acid, 1,8-dihydroxy-3-methylanthraquinone—occurring in the above-mentioned plant products are related to chrysazin (1,8-

dihydroxyanthraquinone, 10, 12), which on oxidation does not yield phthalic acid (8).

Chrysazin (Istizin) has also laxative properties.

Procedure

A suspension of 0.5 to 1 gram of the powdered sample in 20 cc. of a freshly prepared solution of sodium bicarbonate is shaken in a separatory funnel three times with ether, using 25 cc. for the first and 15 cc. for each subsequent extraction. The combined ethereal extracts are washed and evaporated to dryness.

The residue, containing phenolphthalein and the anthraquinone derivatives originally present, is dissolved in 20 cc. of 10 per cent potassium hydroxide and the red to purple solution is oxidized by successive additions of 30 per cent hydrogen peroxide, preferably in a beaker or a porcelain casserole, heating gently over a low flame. An Erlenmeyer flask should not be used for this process, because of foaming and a tendency of the alkaline solution to creep.

The solution is allowed to settle in the cold. A purplish sediment of alkali salts of anthraquinone derivatives (3, 15), if present, is removed, and the alkaline solution is cooled with ice and acidified with an excess of dilute sulfuric acid.

Effervescence and a change of color to colorless or yellow take place. The solution is extracted with three successive portions of ether, using 20, 15, and 15 cc., respectively. The combined ethereal extracts are washed and evaporated first in a casserole to a small volume at room temperature and finally to dryness in a Pyrex tube surrounded with water at about 60° C. The residue in the test tube is heated with an excess of resorcinol in a metal bath at 180° to 200° C. for 20 minutes, or at boiling temperature for 5 minutes over a small flame. No condensing agent is used (9, 14).

The resulting melt is dissolved in about 5 cc. of potassium hydroxide and diluted with water. According to the quantity of phenolphthalein present in the original sample, a more or less pronounced green fluorescence will be observed.

The presence of 5 to 10 gamma of phenolphthalein in the original mixture can be detected by this procedure.

Cascara sagrada tablets to which succinic acid and oxalic acid had been added gave negative fluorescence tests.

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A Glass Vapor-Density Balance

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VAPOR-density balances are very useful in connection with apparatus used for the study of gases. A very satisfactory design is shown in Figure 1. It is made entirely of Pyrex glass, has a vapor jacket to maintain constant temperature during measurements, and has been found to be as sensitive as the pressure can be read on an ordinary mercury manometer.

The beam can be adjusted for center of gravity by careful bending, and the balance can be adjusted by carefully pulling off or adding small pieces of glass. If this is done at ordinary laboratory temperatures and pressures, the balance when assembled will balance in pure oxygen at about atmospheric pressure, when the vapor of boiling acetone is used in the jacket. The increase in temperature approximately com-

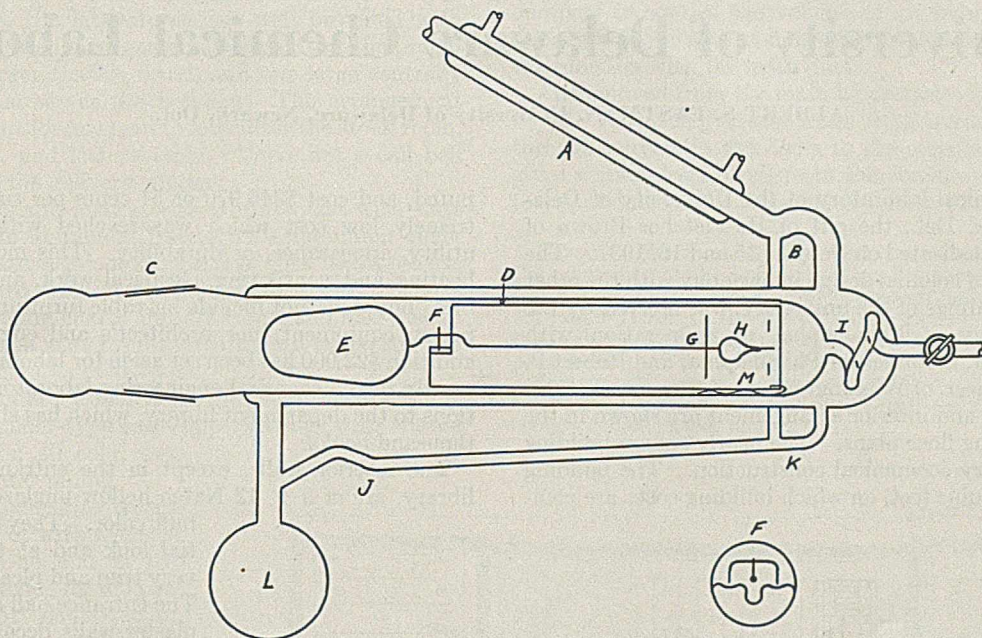


FIGURE 1. DIAGRAM OF GLASS VAPOR-DENSITY BALANCE

- | | | |
|---------------------------|-----------------|----------------|
| A. Water-cooled condenser | F. Bearing | K. Return tube |
| B. Trap | G. Cross rod | L. Flask |
| C. Ground joint | H. Counterpoise | M. Springs |
| D. Support tube | I. Spiral | |
| E. Closed bulb | J. Liquid trap | |

The beam is made of rod about 1 mm. in diameter, and is about 17 cm. long. At one end is a closed bulb, *E*, which is as thin as it can be made and yet have sufficient mechanical strength. It tapers toward the far end, so that it does not strike the containing wall during swings. The bearing at *F* is made of thin rod which terminates in two sharp but fire-polished points. The cross rod, *G*, serves to stop the swings when its ends strike the wall of the support tube and prevents the bulb with its greater surface from making contact with the wall. The counterpoise, *H*, terminates in a pointer.

The support tube, *D*, about 35 mm. in outside diameter, makes a close but not tight fit in the inner tube, and is prevented from rotating by springs of flat metal, *M*, between it and the tube wall. The support is made by tearing a slot in the tube more than half way around and about 1 cm. from the end and shaping with carbon rods. It contains shallow depressions in which rest the bearing points. The inner tube, about 38 mm. in outside diameter, terminates at one end in the large ground joint, *C*, and at the other in a short spiral, *I*, which extends through the end of the outer tube and becomes the connecting tube to whatever apparatus the balance is attached. The outer tube, about 51 mm. in outside diameter, is connected on the lower side to the flask, *L*, by means of two tubes, one for vapor and a return tube, *K*, for liquid, and on the upper side to a water-cooled condenser, *A*. A shallow trap, *B*, and drain return the condensed liquid without its flowing back into the jacket. *J* is a liquid trap.

pensates for the increase in density of oxygen over air. It is desirable to cover the outer tube with a thin coating of asbestos paper for heat insulation except for places at which to observe the pointer and bearings. A telescope with cross hairs is convenient for observing the pointer. The center of gravity can be adjusted so that a difference of pressure of 1 cm. of mercury at the balance point will cause the beam to change from its extreme upper position to its extreme lower position. This gives a precision of readings comparable with the precision with which a mercury manometer can be read, or in the region of 500-mm. pressure an accuracy of 0.2 per cent.

This device has been found very useful in determining the molecular weights of unknown gases, and in following the course of distillation of a mixture containing a homologous series of compounds having a number of isomers. Cuts can be made in the distillation at constant molecular weight rather than at constant temperature. This balance has been found to retain its calibration over periods of months.

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The University of Delaware Chemical Laboratory

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THE new chemical laboratory of the University of Delaware, Newark, Del., the gift of H. Fletcher Brown of Wilmington, was dedicated on October 15 and 16, 1937. The building, which is of colonial design in harmony with the other colonial brick buildings of the university, was erected by the Ballinger Company of Philadelphia in coöperation with Charles Z. Klauder, architect, of Philadelphia, and Robert P. Schoenijahn, engineer, of Wilmington.

The size, shape, and interior arrangement are shown in the three accompanying floor plans. The nearly square building makes possible very economical construction. The building contains 680,000 cubic feet, on which building costs are com-

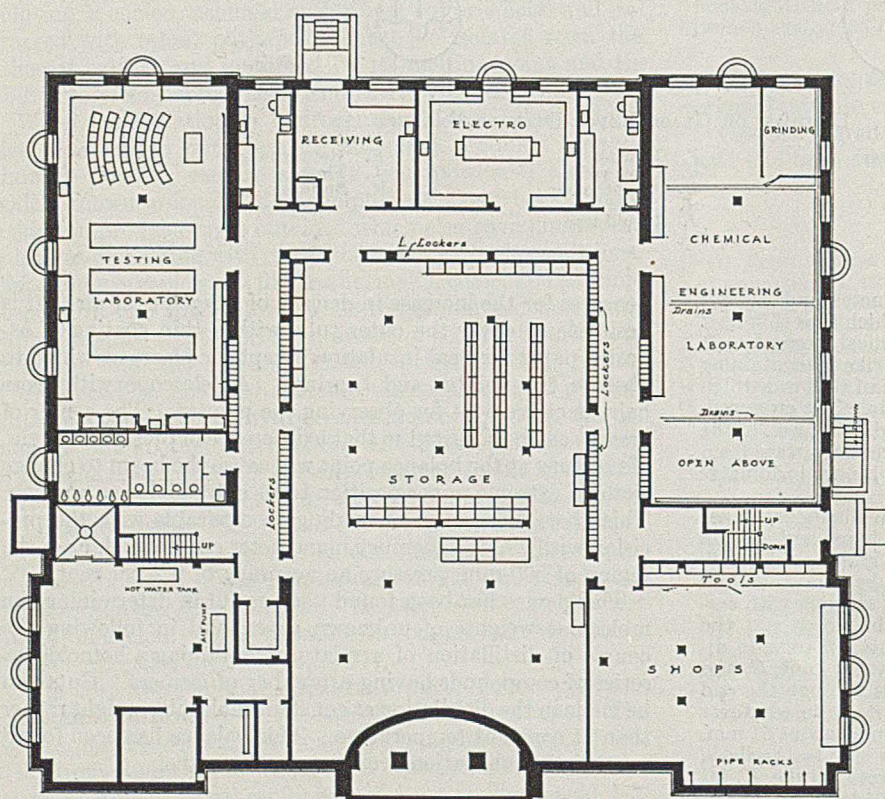
puted, and cost \$346,970 or 51 cents per cubic foot—an extremely low cost which was reached without sacrifice of utility, appearance, or durability. This includes plumbing, heating and ventilating, electrical work, and laboratory tables, but does not include movable furniture, portable laboratory equipment, nor architect's and engineer's fees. In addition \$22,000 has been set aside for laboratory equipment, mostly in the chemical engineering laboratory, and for additions to the department library, which has shelf room for two thousand books.

The interior walls, except in the entrance hall and the library, are of 5 × 12 Natco hollow unglazed tile of a light buff color. They have a substantial look and at the same time a very trim and pleasing appearance. The entrance hall and library have plaster walls decorated to match. The hall or lobby has several built-in, illuminated aluminum show cases, with glass shelves, for the exhibition of material of scientific or technical interest.

The floors are of brick in the entrance hall, linoleum in the library, and concrete in the chemical engineering laboratory. In the laboratories, class rooms, and halls the floors have a special hard-finish asphaltum top, about 1 inch thick, applied hot, over the concrete. Acoustic ceilings are used in the library, classrooms, and lecture room.

The building has more than the usual number of service outlets, and the plumbing, heating and ventilating, laboratory furniture, chairs, and fixtures are of the best quality and workmanship obtainable. Every effort was made to have the laboratory satisfactory in every detail.

The laboratory furniture is of steel, with soapstone desk tops and sinks, and is finished in olive-green to match the steel office furniture. All the shelves, drawers, and lockers



GROUND FLOOR PLAN

in the laboratories and stock rooms have been lined with Sisal-kraft tar paper, bent up at the sides and ends to form a shallow, water-proof tray. The bottom of this tray is covered with a sheet of thick gray lining paper, which is absorbent and may be easily replaced. The tar paper may be purchased of any dealer in roofing paper, and the lining paper of the Eaton-Dikeman Company. The paper linings were suggested by Dr. Foulk of Princeton University.

Each desk in use by students beyond the freshman year has a long drawer for burets and condensers, as well as a pencil tray in each large drawer. The shelf in the cupboard below does not extend all the way to the front, thus providing space for tall bottles and ring stands. All laboratory desks, and the lockers on the ground floor, are provided with master-keyed combination padlocks.

A feature of the building is the large amount of storage available. All the space under the lecture room and lobby is for rough storage, the laboratories are well provided with shelving and cabinets for reagents and apparatus, the preparation room is larger than is usual, and one large centrally located stock room serves the building. The arrangement makes it convenient for one man to look after the stock room, preparation room, and lecture table. There are a call bell and a mail slot at the delivery window.

Both classrooms and laboratories are provided with slate blackboards, set in aluminum frames with aluminum chalk trays. In each case, a 2-foot section is of cork board for use as a bulletin board. Every blackboard has sliding hooks at the top for hanging charts and drawings, and also a strip of cork board, 1-inch wide for use with thumb tacks, set into the top of the frame.

The distilled water system is of aluminum. Streamline copper pipe and solder-type cast-copper fittings with special valves are used on all cold, hot, and circulation water piping.

The chemical engineering laboratory is 71 × 28 feet with windows on two sides. One end is two stories high, to provide for the two-stage evaporator, distillation column, absorption tower, and other relatively tall equipment. The balcony or gallery is for gravity flow experiments, and a traveling crane is located over the balcony and two-story portion. Numerous outlets for high-pressure steam, air, gas, hot and cold water, electric power, direct current, etc., are located at the columns and in each bay in order to provide flexibility in use.

Two of the offices have private laboratories attached, but twelve other rooms are intended to serve as combination offices and private laboratories. The larger of these have two laboratory tables, fitted with gas, air, water, steam, suction, alternating and direct current, a hood, office desk, two chairs, bookcase, filing cabinet, and wardrobe.

The building was planned to be run by a staff consisting of two janitors, one mechanic, one stock-room man, and one secretary-librarian. During one year of use this has proved to be satisfactory.

Ventilation

The main laboratories and all research rooms are connected to systems of mechanical exhaust ventilation. There are five exhaust systems, each having sheet-lead ducts with separate branches and risers leading from the hoods, and also general exhaust ducts with outlets at both floor and ceiling to remove both heavy and light gases from the room. In general the ducts extend up through the building, within the double partitions of the corridor walls, into the attic space, where they connect to the main horizontal ducts, going to their respective fans. The fans have sheet-lead discharge ducts extending into lead-lined masonry vent chimneys.

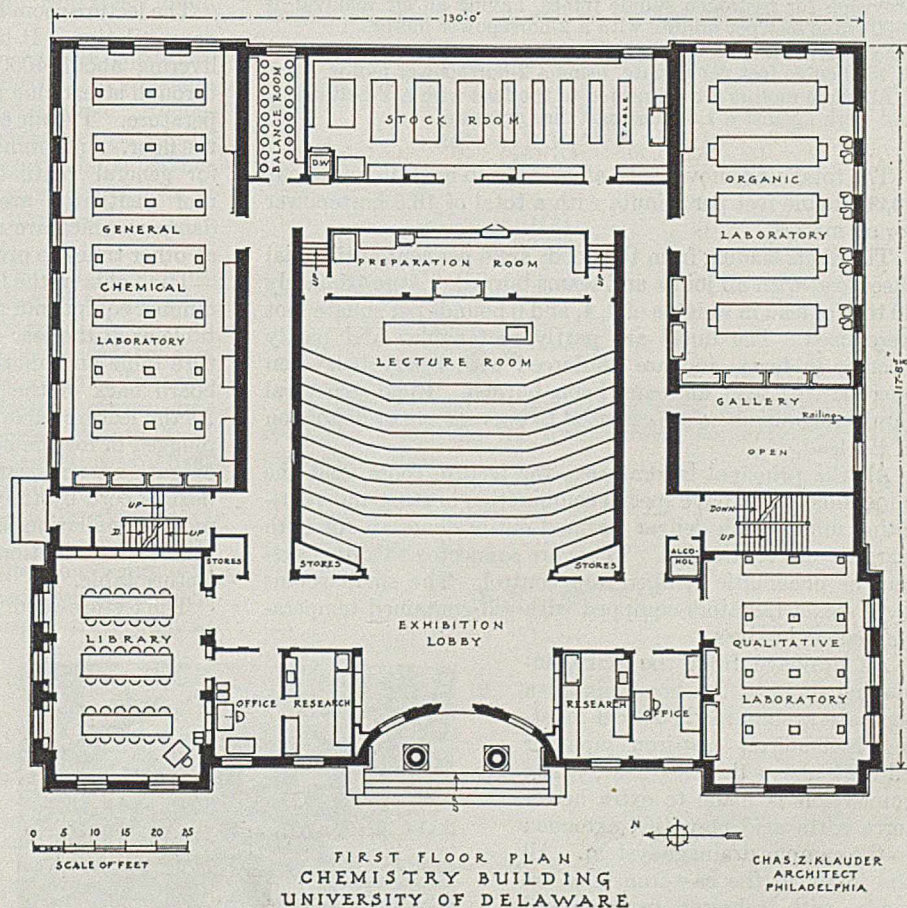
There is a down-draft hood on each desk in the general and qualitative laboratories, and all the laboratories, including the private rooms, are provided with hoods, some of the open-front type. The table and wall hoods are fitted with local dampers to control the volume of air removed. The room ducts are fitted with volume-control dampers in the attic at the junction with the main ducts.

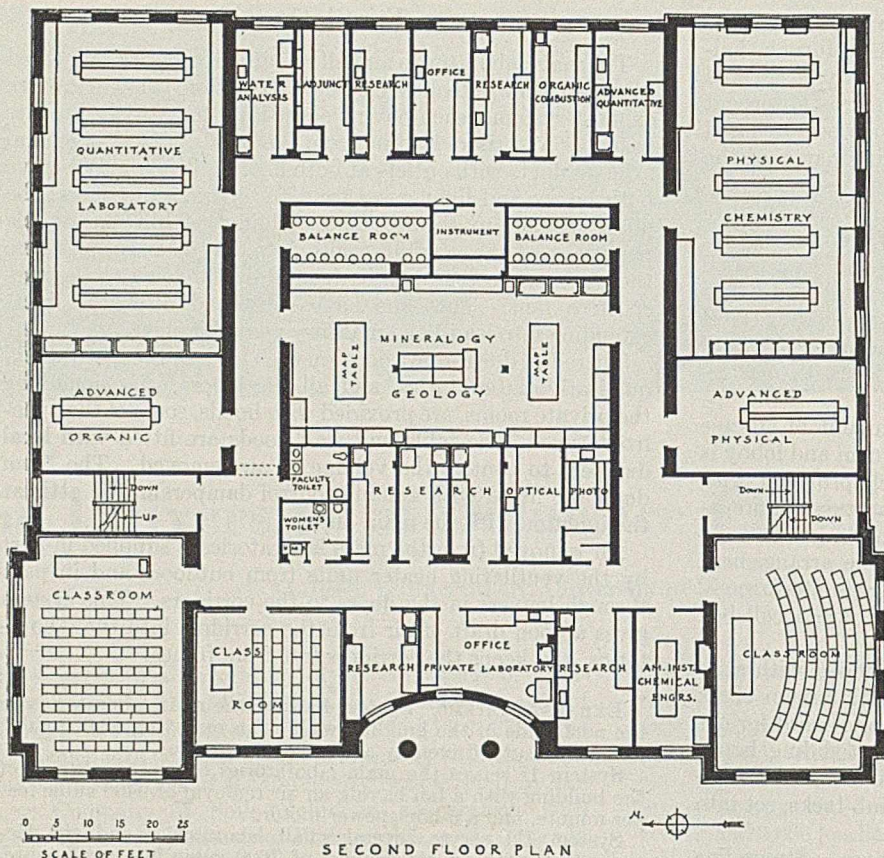
Air removed from the main laboratories is supplied in part by the ventilating heater units from outdoors and in part through louvers in the doors to the corridors. This system gives a good draft of air from the corridors into the laboratories, and keeps the corridors free from fumes.

EXHAUST SYSTEMS. System I serves the main laboratories on the north side of the building with a fan removing 12,000 cubic feet per minute, driven by a 5-horsepower motor.

System II serves the main laboratories on the south side of the building with a fan having an air removal of 9400 cubic feet per minute, and a 5-horsepower motor.

System III serves several small laboratories and the lecture room, with an air removal of 7600 cubic feet per minute, using a 3-horsepower motor.





System IV serves the qualitative laboratory only, with special provision for hydrogen sulfide fumes, having an air removal of 4300 cubic feet per minute with a 2-horsepower motor.

System V serves a number of small rooms with an air removal of 4300 cubic feet per minute, using a 2-horsepower motor.

All these motors are connected to the fans with a V-belt drive, and work against a 1.5-inch resistance pressure.

The total air removal with all systems in operation is about 36,000 cubic feet per minute with a total of 16.5 horsepower for all motors.

The ducts leading from the hoods are 6 per cent antimonial sheet lead with all joints and seams burned. Approximately 30 tons of lead in weights of 3, 4, and 6 pounds per square foot were used. The ducts are partly rectangular and partly circular in form, and are reinforced with heavy band-iron overlaid with lead, all seams being burned. Rigid structural supporting members are essential to prevent sag or distortion of the lead.

All the principal laboratories, the lecture room, and the mineralogy room have special combination heating and ventilating units which deliver warmed out-of-doors air for both warmth and ventilation. These are connected to a dual system of pneumatic temperature control. The small rooms have steam radiators equipped with self-contained temperature-control valves.

All drainage from the sinks, including those in the hoods, is by a separate system made of acid-resisting high-silicon cast-iron pipe for all work above the basement, where connection is made to extra heavy terra cotta acid clay tile, extended to the campus drainage system. All the joints in the cast-iron lines are made with asbestos gaskets and

caulked lead. The tile pipe is made up with hot-poured bitumastic acid-resisting compound.

Electrical Service

Electrical service for the building is taken from the campus underground distribution system, 2300-volt, 3-phase, 60-cycle. Transformers provide for 120- to 208-volt, 3-phase, 4-wire distribution for light feeders and 208-volt, 3-phase, 3-wire distribution for power requirements. The power and light panels are dead-front, "no-fuse," circuit-breaker type.

The general lighting is by means of ceiling lens-type lighting units in metal boxes, some of which are surface-mounted against the concrete ceilings and some set flush in the hung ceilings.

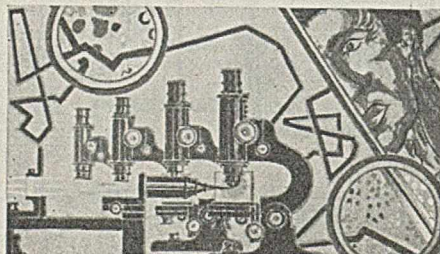
Direct current is distributed to all the laboratories by a separate system, which includes two 3-kw. motor-generator sets, a storage battery, and special distribution panels of plug-bus cordless type, capable of providing direct current in 2-volt steps from 2 to 24 volts and also at 110 volts.

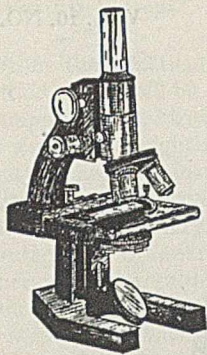
Lecture Room

The lecture room has 270 seats, and is without outside light or ventilation. It has a separate heater unit in the attic delivering about 4000 cubic feet per minute of outdoor air through streamline grilles, to maintain a uniform room temperature. The air exhaust is by gravity through outlets near the floor. In summer the unit may be operated at high speed for general ventilation. The air-intake duct and gravity roof ventilator are fitted with pneumatically controlled dampers which are open when the system is in use and closed at other times to prevent unnecessary loss of heat.

The lights in the lecture room are controlled by Thyatron dimmer equipment, which may be operated either at the lecture table or at the rear of the room. Special lights over the lecture table and another set of lights to illuminate the blackboard back of the table may be independently controlled. At the lecture table a push button on a flexible cord may be plugged in for the use of a speaker showing lantern slides, to operate a small signal light, which may be plugged in on a flexible cord by the lantern operator. There is also a sound movie installation for 16-mm. film, and a spotlight for special intense illumination of limited areas of the blackboard or lecture table.

The lecture-room floor is sloping and the preparation room is at the lower level. By raising the center section of the blackboard back of the lecture table, apparatus may be passed to and from the preparation room where lecture material is prepared and stored. This room is a fully equipped laboratory as well as store room.





Microchemistry

Paper as a Medium for Analytical Reactions

A Method of Applying Reagent Papers to Large Volumes of Solution

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A DISTINCT advantage of the use of slightly soluble or "fixed" impregnants in reagent papers is the localization of the reaction in or near that area receiving the liquid under test. The reaction product thus concentrates on the fibers of a restricted area while the liquid, depleted of the ion precipitated, flows away. In the first article of this series (1), the application of this principle to "spot" tests was discussed. The solution is introduced from a capillary orifice, liquid flow being maintained by absorptive spreading in the surrounding paper. The volume handled in this manner cannot conveniently exceed 0.1 or 0.2 cc. For most purposes, especially where the test drop represents the final product of a series of separations and its dilution is not great, this quantity is sufficient.

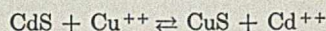
There remains, however, the case where the substance under test is present in very low concentration, and consequently a large volume of solution must be taken. Reduction of this volume may be impracticable because of the high concentration of other salts with which the substance sought may be associated, for example, as an impurity. It may be undesirable because of the loss of time involved, as in the examination of waters or soil extracts.

Under suitably chosen conditions, it is still possible to effect the removal of microgram quantities of an ion from large volumes of solution by means of reagent papers. In the method here reported the solution is caused to flow through a restricted area of the paper at a controlled rate. The paper is held across the liquid stream between two tightly compressed flanges. Reaction occurs essentially at the coated fiber surfaces and the product is retained by fixation thereon. When a color change results, direct comparison of the colored area with standards identically prepared may provide an approximation of quantity. If more precise determinations are required or the simultaneous removal of more than one ion by the paper necessitates subsequent separation, ashing or digestion of the spot then permits operations on a true micro scale.

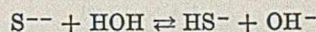
Three fundamental requirements must be met if a reaction is to be used in the proposed manner:

1. The impregnating reagent must be sufficiently insoluble to withstand the action of the large volume of solution flowing through a small area of the paper.
2. Sufficient difference must exist between the solubilities of reagent and reaction product to ensure reasonably quantitative precipitation of the ion sought.
3. The reaction product must be capable of immediate fixation on the fibers of the paper.

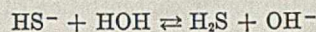
Consider, for example, the reaction between cadmium sulfide paper and copper ion:



Practical use of this reaction for the separation of traces of copper is discussed below. For present purposes, suppose a liter of the test solution is passed through a small area of paper, impregnated with cadmium sulfide, and that this percolation yields an outflowing solution which is saturated with cadmium sulfide. The dissolved cadmium sulfide dissociates to give equivalent concentrations of cadmium ion and sulfide ion, but the latter reacts with water to give largely hydrosulfide ion and un-ionized hydrogen sulfide:



and



where (at 18° C.)

$$\frac{[\text{S}^{--}] \times [\text{H}^+]}{[\text{HS}^-]} = 1 \times 10^{-16} \quad (1)$$

and

$$\frac{[\text{HS}^-] \times [\text{H}^+]}{[\text{H}_2\text{S}]} = 9 \times 10^{-8} \quad (2)$$

Equations 1 and 2 take into account the acidity of the solution. Assuming the hydrogen-ion concentration to be 0.01 molar, from 1,

$$[\text{HS}^-] = 10^{13} [\text{S}^{--}] \quad (3)$$

and, combining 2 and 3,

$$[\text{H}_2\text{S}] = 10^{18} [\text{S}^{--}] \quad (4)$$

Now, at 18° C.,

$$[\text{Cd}^{++}] \times [\text{S}^{--}] = K_{\text{CdS}} = 3.6 \times 10^{-29} \quad (5)$$

But,

$$[\text{Cd}^{++}] \approx [\text{CdS}] \quad (6)$$

the molar concentration of dissolved cadmium sulfide, and

$$[\text{CdS}] \approx [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{--}]$$

or

$$[\text{S}^{--}] \approx [\text{CdS}] - [\text{H}_2\text{S}] - [\text{HS}^-] \quad (7)$$

Combining Equations 3 and 4 with 7,

$$[S^{--}] \approx [CdS] - 10^{18} [S^{--}] - 10^{18} [S^{--}]$$

or

$$[S^{--}] \approx \frac{[CdS]}{10^{18}} \quad (8)$$

From 5, then,

$$[Cd^{++}] \times [S^{--}] \approx \frac{[CdS]^2}{10^{18}} \approx 3.6 \times 10^{29}$$

or

$$[CdS] \approx 6 \times 10^{-6} \quad (9)$$

Combining 8 and 9,

$$[S^{--}] = \frac{[CdS]}{10^{18}} = \frac{6 \times 10^{-6}}{10^{18}} = 6 \times 10^{-24} \text{ mole per liter}$$

in a saturated solution of cadmium sulfide.

In actual practice, however, the molar concentration of sulfide ion available is expressed by

$$q \times 6 \times 10^{-24} \text{ mole per liter}$$

where q is a fractional factor denoting the degree of saturation attained by the outflowing solution. This will depend on the conditions maintained in practice, chief among which are the rate of flow, the area of paper exposed, and the nature of the layer being precipitated over the cadmium sulfide-coated fibers.

Now assume the solution to contain a small amount of copper. As the copper ions enter the cadmium sulfide region copper sulfide is precipitated to satisfy the mass action law expressed in the solubility product:

$$[Cu^{++}] \times [S^{--}] = K_{CuS} = 8.5 \times 10^{-45} \quad (10)$$

But, since

$$\begin{aligned} [S^{--}] &= q \times 6 \times 10^{-24} \\ [Cu^{++}] &= \frac{1.4 \times 10^{-21}}{q} \end{aligned} \quad (11)$$

where $[Cu^{++}]$ is the molar concentration of copper ion remaining in solution.

Thus, if a solution containing traces of copper attains 1 per cent saturation ($q = 0.01$) with cadmium sulfide, the copper remaining unprecipitated will be:

$$[Cu^{++}] = \frac{1.3 \times 10^{-22}}{0.01} = 1.3 \times 10^{-19} \text{ mole per liter}$$

or 8.3×10^{-12} microgram per liter. Even if the degree of saturation attained were only 0.001 per cent, the recovery of 1 mg. of copper from a liter of solution would be quantitative enough for practical purposes.

When the solution is passed through a second paper, however, it will contain an excess of cadmium ion, equivalent in quantity to the copper precipitated on the first paper. This will repress the solubility of the cadmium sulfide at the second paper and reduce the sulfide-ion concentration available.

In the present case, the difference between the solubilities of copper sulfide and cadmium sulfide is so great that even this will not materially decrease the efficiency of recovery. When circumstances are less favorable, however, as will be the case in many other reactions, it is important to emphasize the necessity of adjusting conditions for as complete removal as possible of the ion under test by the first paper.

In the preceding discussion, the factor q was introduced because of the realization that only an infinitely slow rate of flow would permit equilibrium conditions to be approached. In the example chosen, efficiency of recovery is clearly dependent on factors influencing attainment of equilibrium

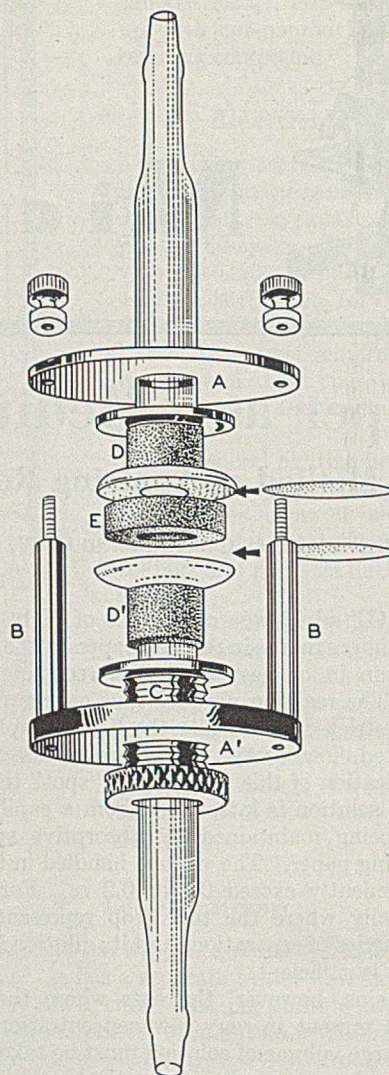


FIGURE 1. DETAILS OF FLANGE AND CLAMPING ASSEMBLY FOR HOLDING IMPREGNATED PAPER DISKS IN FLUID STREAM

rather than on the conditions of that equilibrium. Were saturation of the outflowing liquid with the impregnating reagent actually attained, q would, of course, become unity.

When relatively small differences between the solubilities of reagent and reaction product leave little working margin, it becomes increasingly important to bring q as near to unity as possible. To accomplish this, flow should be reduced to the lowest practicable rate, while the exposed area of the paper should be as large as the estimable range of spot densities or as subsequent manipulations will allow.

The texture of the paper is also important. Very loose papers will have relatively large pores, through which the bulk of the solution will pass without opportunity for its ions to meet those of the precipitant or for the product formed to become fixed completely on the fibers. Thick papers are required to afford sufficient reagent, to break up the capillary channels, to prolong the contact period, to ensure uniformity, and to provide sufficient mechanical strength. Of those tried, C. S. & S. No. 598 approaches the type which would seem desirable. Its thickness and wet strength are satisfactory. A somewhat closer texture and greater uniformity of pore size would improve its value in this work, however.

From the practical standpoint, it would seem that the method might still be applied advantageously to many types of impurity and "trace" analyses, even though recovery of the ion sought might reach only 90 or 95 per cent. Its simplicity guards against the manipulative losses which often make the more conventional approaches so uncertain that reproducible recovery of even such percentages cannot be counted on. Standardization of conditions for the reagent paper method results, at least, in a reproducible recovery, upon the basis of which estimations of quantity may be made. In a sample of nickel containing 0.005 per cent of copper, for example, it is seldom that the recovery of 0.0045 per cent would not be entirely acceptable.

Apparatus

The apparatus used to confine the flow of large volumes of liquid through small definite areas of the impregnated papers is shown in Figures 1 and 2.

The unit consists of a pair of glass tubes, the ends of which terminate in heavy face-ground flanges, the plane of grinding being exactly normal to the axis of the tube.

The flange openings have the same bore as that of the tube. (Such flanges may also be turned from Pontalite rod, thereby obtaining the advantages of accurate machining.) The paper is inserted between the flange faces, and pressure is applied by the clamp assembly shown. This consists of two brass plates, *A* and *A'* (Figure 1), separated by posts *B*. One of the flange tubes passes loosely through the hole in plate *A*; the other extends through the bore of the tightening sleeve, *C*, which is in turn threaded through a hole in plate *A'*. By tightening *C*, the flanges are forced together. Between the flange shoulders and the metal parts are heavy rubber compression cushions, *D* and *D'*, which prevent breakage by providing the necessary elasticity. To prevent twisting of the flanges when the tightening sleeve, *C*, is turned, a graphite-lubricated washer is placed between it and the rubber cushion.

When it is necessary to pass the liquid through several paper disks in succession, a separation of these disks is usually desirable, especially when the first disk is unimpregnated and serves only to filter the solution. One or more hard-rubber separator rings may then be inserted between the flange faces. These rings have the same bore as that of the flanges and may be provided in various thicknesses to permit

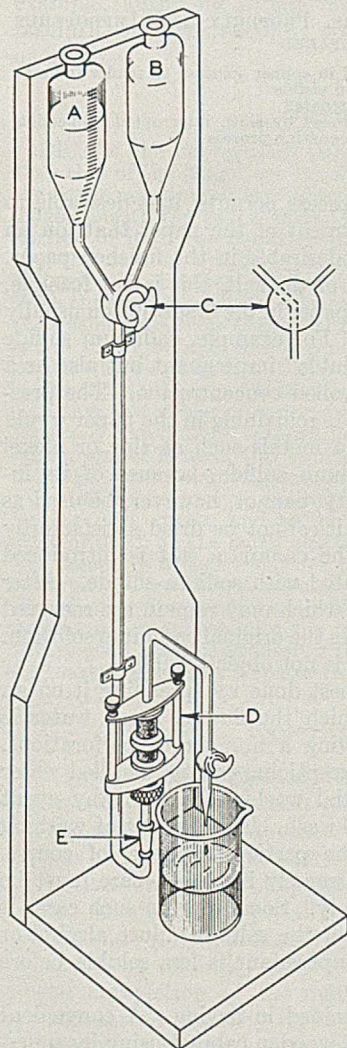


FIGURE 2. APPARATUS ASSEMBLY FOR RECOVERY OF TRACES FROM DILUTE SOLUTIONS ON IMPREGNATED DISKS

- A. Reservoir containing solution
- B. Reservoir containing wash liquid
- C. 3-way stopcock
- D. Flange-clamping assembly
- E. Standard ground-glass joint to facilitate removal of clamping assembly

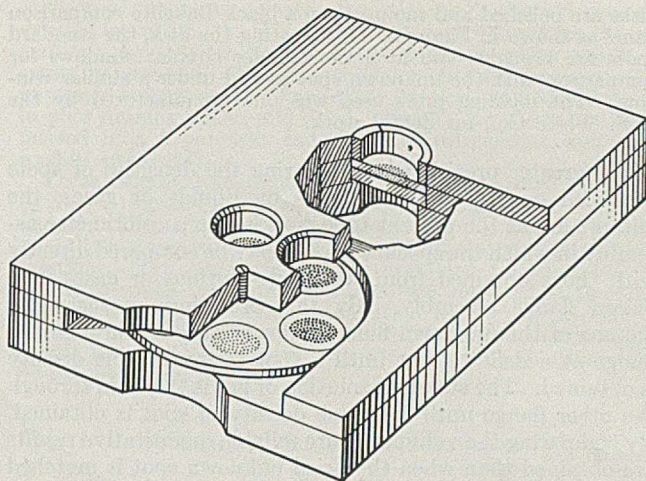


FIGURE 3. STANDARD SPOTS MOLDED IN LEUCITE WITH DETAILS OF COMPARISON BLOCK

variation of the distance between the papers. They provide a convenient alternative to the use of two or more separate flange and clamping assemblies. The rings are soaked in hot paraffin for several minutes to seal the surfaces coming in contact with the solution as a protection against adsorption or possible reaction with the ions being precipitated in the paper. When the conditions for a particular reaction are not already precisely established, or the quantities involved are not known, it is advisable to use several papers in series, since then completeness of removal in the first paper may be checked by examination of those that succeed it.

For approximation of quantity by comparison of spot densities, it is convenient to have prepared a series of standard spots made under conditions identical with those of the test. The permanent preservation of these standard spots often presents a problem because of deterioration brought about by the action of air, light, and moisture. Dipping in paraffin is commonly practiced, but this form of protection necessitates further mounting. For sulfide spots the authors have tried the experiment of molding the paper disks in Leucite. Three months after preparation the spots appear to be entirely stable; a more definite report on their stability will be given in a subsequent publication. The method is as follows:

In a shallow cylindrical mold (7.5 cm., 3 inches, in diameter) a layer of Leucite molding powder sufficient to give a finished disk 0.16 cm. (0.06 inch) thick is placed. Two such disks are formed at 175° C., and under 2700 to 4500 kg. (6000 to 10,000 pounds) pressure. The papers with the spots are then placed in a symmetrical arrangement on the face of one of the disks, after which the other disk is placed over it. The two disks with the spots between them are now returned to the mold and heated at 125° C. under 4500 kg. (10,000 pounds) pressure for 0.5 hour. On removing, a perfect sealing of the papers within a disk of the transparent material will have been accomplished. Such

disks are polished and mounted on a black Bakelite comparison panel as shown in Figure 3. By rotating the disk, the standard spots are brought, two at a time, under circular windows for comparison with the unknown spot placed under a similar window. The molding press used was one manufactured by the S. S. White Co., for dental work.

For greater precision in comparing the densities of spots produced on paper disks, either by liquids or gases, the authors are at the present time working on a colorimeter assembly in which the specimen spots may be compared directly with those obtained from standard solutions or gases in a paired flange assembly. By this procedure, a measured volume of the unknown fluid is allowed to pass through the flange at a definite rate until a spot of measurable density is obtained. The standard solution or gas is then run through the other flange until the same density of spot is obtained. By comparing the volumes, more reliable quantitative results are obtained than when the dried unknown spot is matched against a series of standards. A report is expected on this work in the near future.

Preparation of Reagent Papers

Difficultly soluble compounds may be incorporated in the paper in two ways. When the water-insoluble reagent is soluble in a suitable organic solvent such as alcohol, acetone, benzene, or ether, the process is simple—that of dipping, blotting off the excess, and drying. Substances such as α -benzoinoxime and α -benzildioxime are examples. Fixed inorganic impregnants, for which such solvents do not exist, must be precipitated directly on the paper fibers. This is generally done by successive immersion in solutions of the substances which react to give the desired difficultly soluble product. In a few cases, however, a substance may be introduced into the paper in soluble form and by exposure to gas or vapor, by evaporation, or by the action of physical agencies such as light or heat, may be converted to the final "insoluble" product.

When successive dipping is the method, the density and uniformity of impregnation are controlled, respectively, by the quantity and distribution of one of the two reacting substances introduced by the first immersion. The excess liquid is removed by passing the paper through a small wringer with pressure between the rolls maintained at a definite value. To ensure complete uniformity, the paper must be fed into the wringer at a uniform rate. Between immersions, the paper is dried. If this is not done, the second solution will not be taken up by the paper, and precipitation of the reagent, instead of taking place at the fiber surfaces, will be superficial, yielding a nonadherent product which floats away from the paper surface.

The exact technic of immersion is important. The paper, cut to a size permitting easy manipulation, is lowered into the solution at a fairly rapid, uniform rate. If this practice is not followed and the operator's hand hesitates for an instant, the solution may rise by capillarity above the level of the liquid in the vessel. When this occurs, the concentration of solute in the advancing wet boundary is usually reduced through adsorption and does not adjust itself to that of the solution when fully immersed. Each time this happens, therefore, a streak on the finished paper results. In the second immersion, the effect is even more marked. Then, if the solution is allowed to rise in the paper, precipitation quickly depletes it of reactive ions, after which the advancing liquid dissolves and carries with it the salt with which the paper was impregnated in the first step. A narrow band, practically devoid of reagent, followed by one of abnormally heavy impregnation just above it, is the final result. Non-uniformity is also caused by changed absorptiveness of the paper along fold or wrinkle lines. Local moistening caused,

for example, by splashing or by wet fingers prevents entry of solution on immersion and leads to spottiness. On salt-impregnated papers it gives rise to capillary concentrations of the soluble salt and hence spoils completely the chances of obtaining a uniform product. Figure 4 shows such dipping striations on a typical paper.

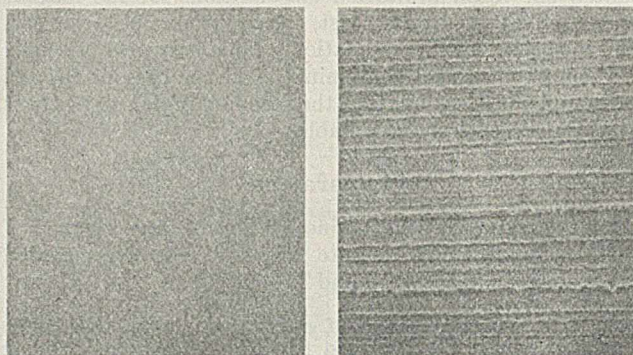


FIGURE 4. REAGENT PAPERS, PROPERLY AND IMPROPERLY PREPARED

Zinc ferrocyanide paper, developed in copper solution to render impregnation visible
 A. Uniform paper, properly impregnated
 B. Paper showing striations produced by slow, interrupted immersion during impregnating process

When the nature of the process permits, it is desirable to incorporate in the first treatment of the paper that ion an excess of which would be undesirable in the finished paper. If, because of the instability of the salt, this is not feasible, then final reimmersion of the paper in the first solution usually accomplishes the same end. For example, cadmium sulfide is used not only as an "insoluble" impregnant but also as a source of sulfide ion of controlled concentration. The presence of traces of sodium sulfide remaining in the paper would defeat the latter purpose and metals such as zinc or nickel might be precipitated. Sodium sulfide, because of its instability and caustic alkalinity, cannot, however, be used as the first impregnant because it cannot be dried satisfactorily on the paper. Therefore, the cadmium salt is introduced first and its sulfide precipitated with sodium sulfide. After washing, traces of the latter which may remain are removed by reimmersion of the paper in the original cadmium solution. A trace of free cadmium ion is not objectionable.

Washing of the paper is best done by spreading it on an inclined glass plate over which the flow of wash water is spread by a glass tube having a number of perforations. Unless the tap water is of exceptional purity, distilled water should be used for the initial washing, and in any event it should be used for the final wash. The amount of washing necessary will vary with the particular paper, of course. When the reagent is not extremely insoluble, care must be taken not to prolong it unduly. Sometimes in such cases it is better to leach out most of the salts in dilute alcohol or other media in which the impregnant is less soluble before applying a final short washing.

Overheating should be avoided in drying. A convenient oven can be constructed of a wooden cabinet using incandescent bulbs as the heating source. The papers should be protected from the strong light by a suitable baffle. The papers in general keep best when in tightly compressed packages away from light and laboratory fumes.

The density of impregnation may be computed approximately from the concentration of the solution in which the paper is first immersed and the liquid capacity of the paper used. The latter value is obtained by weighing a given area

of the dry paper, then weighing the same area after wetting with water and passing through the wringer. From the dry and wet weights and the area, the volume of liquid taken up by 1 sq. cm. of paper is determinable. The concentration of the solution used in the first immersion can then be adjusted to provide the desired density of precipitated reagent in the finished paper.

Papers to be used in the liquid stream should be impregnated as heavily with reagent as is consistent with uniform flow through the fibrous interstices. Such impregnation, therefore, should be accomplished by building up reagent layers on the fiber surfaces rather than by filling the interstices, for in the latter case interference with the flow would lead to channeling and to mottled spots. This desired type of precipitation results only when the paper is dried between immersions. When the impregnant is a colored compound such as cadmium or antimony sulfide, matching of spots, especially when faint, is usually enhanced by removal of the excess reagent. Subsequent treatment of the spot may also make presence of impregnant undesirable. In such cases appropriate treatments which leave the reaction product untouched but dissolve the impregnant may be devised. For example, antimony sulfide may be removed from copper, bismuth, or silver spots by treatment with dilute ammonia or alkali.

Technic

Disks of the impregnated paper, of diameter slightly smaller than that of the flange, are cut with a cork borer. In setting up the flange assembly, it is of course imperative that no air bubbles lodge beneath the paper, since this would prevent exposure of a portion of it to the liquid stream, producing an uneven stain. For this reason, the best practice is to bring the solution in through the bottom of the vertically supported assembly. With the tightening screw released, water is allowed to flow from the washing reservoir (Figure 2) until the rubber connecting tube is free of air bubbles and a continuous column of liquid is obtained which overflows at the lower flange.

The moistened paper is then laid over this flange, after which a further few drops of water are allowed to exude in order to expel any fine bubbles trapped beneath the paper. If the hard-rubber spacer is used, this is held against the lower flange with the fingers and water is again admitted until it fills to overflowing, when the second paper is put in place. The operation is repeated for the next spacer and so on. Finally, the upper flange is brought down on the paper and the clamping sleeve is tightened. The assembly is then ready for passage of the solution from its reservoir. Care should naturally be taken to ensure freedom from dust or fine precipitates which would be filtered out on the reagent paper and obscure the reaction product. In fact, it is always good practice to insert a filter paper disk, separated from the reagent papers by a spacer ring, to act as a cleaner.

Experimental

The writers have confined the present introductory studies largely to the precipitation of copper on cadmium sulfide paper, as a typical application. Reactions with metals such as copper, silver, mercury, bismuth, and lead, involving separation on papers impregnated with light-colored insoluble sulfides, are especially suited to this technic. Both reagent and reaction product have high degrees of insolubility, yet sufficient solubility differences often exist to ensure essential completion of the metathetical reaction. Further, the widespread necessity for determining minute amounts of such metals in great dilutions would seem to justify this starting point. In the writers' laboratory the examination of waters associated with corrosion problems, as well as the determination of impurities in nickel, aluminum, and other metallurgical products, has given first importance to these reactions.

COPPER REMOVAL ON CADMIUM SULFIDE PAPER. Sheets of C. S. & S. No. 598 paper are first immersed in a 15 per cent

solution of cadmium acetate, passed through the wringer, and dried in warm air. In this and the following operations, the precautions discussed in the general part of this paper are to be carefully observed. The dried cadmium acetate sheets are then immersed in 5 per cent sodium sulfide solution, washed thoroughly in pure running water, and dried. Finally the sheets are reimmersed in a 5 per cent cadmium acetate solution and again washed and dried.

Three disks of the cadmium sulfide paper, separated by 0.6-cm. (0.25-inch) spacers, were clamped between flanges of 1-cm. diameter. Through such arrangements were passed varying quantities of water, 0.01 molar acid, and 0.1 molar sodium acetate solutions. The papers were then examined to determine the extent to which the cadmium sulfide was depleted in the areas exposed to the flow. The examination was aided, in doubtful cases, by conversion of the cadmium sulfide to brown-black copper sulfide by immersing the spot in copper sulfate solution. The results are shown in Table I.

TABLE I. STABILITY OF PAPERS
(At 20° C.)

No.	Fluid	Volume	Flow Rate	Depletion of CdS Impregnant	1st disk	2nd disk	3rd disk
		Cc.	Cc./min./sq. cm.				
1	Water	1000	1	Slight	None	None	None
2	0.01 molar H ₂ SO ₄	1000	20	Marked	Considerable	Slight	Slight
3		1000	1	Practically complete	Moderate	None	None
4		500	1	Marked	Slight	None	None
5		100	1	Slight	None	None	None
6	0.01 molar H ₂ SO ₄ +0.1 molar NaAc	1000	1	Appreciable	Very slight	None	None
7		500	1	Slight	None	None	None

These experiments show the effects of acidity and rate of flow on solution of the cadmium sulfide impregnant. As might well be reasoned, the slower the flow, the more nearly saturated is the outflowing liquid and the more cadmium sulfide is dissolved. With water, solution is so slight, even at the slow flow rate of 1 cc. per minute per sq. cm., that a liter removes only negligible quantities from the first paper, the others being unaffected. Hundredth-molar acid naturally dissolves much more. A liter at the slow rate almost entirely removes the cadmium sulfide from the first paper, while the second shows appreciable loss of color; the third is relatively unaffected. When the 0.01 molar acid is passed at the fast rate of 20 cc. per minute per sq. cm., solution of the cadmium sulfide is still appreciable, but occurs to a much smaller extent than at the slow rate. Moreover, of the cadmium sulfide dissolved, far less is removed from the first paper and a much greater proportion is removed from the second. Even the third paper is visibly affected. At slow rates of flow, saturation seems to be practically attained at the first paper and the others are unaffected until most of the impregnant in the first paper is removed. Rapid flow, on the other hand, prevents anything approaching equilibrium at the first paper, so that the impregnant is to some extent removed by the unsaturated solution from the succeeding papers. Rate of flow, therefore, is certainly an important factor.

Despite the fact that acid in 0.01 molar concentration greatly increases the solubility of the cadmium sulfide impregnant, there is still sufficient of this in the three-paper system to provide for quantitative removal of 50 micrograms or less of copper on 1-sq. cm. areas from a volume of 500 cc. at 1 cc. per minute per sq. cm. Precipitation will be substantially complete on the first paper until enough solution has passed to deplete the impregnant, after which the second paper will receive the copper. However, it is advantageous if the precipitation of practically all the copper or other metal sought can be made to take place on the first paper, especially when the quantity is to be estimated by comparison with standard spots. Since in practice a neutral, unbuffered solution for analysis is troublesome to obtain, control of acidity is logically effected through use of a suitable buffer. In

TABLE II. IMPORTANCE OF RATE OF FLOW

(50 γ of copper in 0.01 molar H₂SO₄, buffered with 0.1 molar sodium acetate)




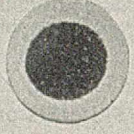


No.	Rate of Flow Cc./min./sq. cm.	Cadmium Sulfide Disk		
		First	Second	Third
1	20			
2	2			

TABLE III. RECOVERY OF COPPER

(20 γ of copper, 0.01 molar H₂SO₄, buffered with 0.1 molar sodium acetate. Flow rate, 2 cc. per minute per sq. cm.)


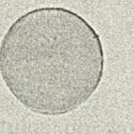



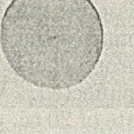
Volume Cc.	Cadmium Sulfide Disk	
	First	Second
10		
100		
1000		

Table I it is evident that 0.01 molar sulfuric acid, when buffered with sodium acetate in 0.1 molar concentration, has little more effect on the cadmium sulfide impregnation than has water under the same conditions. In the succeeding experiments, therefore, the copper solutions were all buffered in this manner.

The rate of flow is important in other respects. If the solution passes through the paper at too rapid a rate, not enough cadmium sulfide is dissolved to provide the concentration of sulfide ion needed for complete precipitation of the copper. Further, insufficient time is allowed for reaction, growth of colloidal particles, and their fixation on the paper. An experiment which demonstrates this is summarized in Table II.

In this experiment the same volume of solution containing the same quantity of copper was passed through the papers at the two widely differing rates of flow. At 20 cc. per minute per sq. cm., recovery of the copper is not complete with three papers. At 2 cc. per minute per sq. cm., practically all is precipitated on the first paper.

Besides the above controllable factors, one which may impair the completeness of removal of the copper on the first paper is excessive channeling. This may be caused by exceptionally large pores resulting from faulty manufacture or by nonuniform impregnation. Very heavy impregnation







may close the finer interstices altogether, diverting the fluid stream at high velocity through the few large ones still open. The impregnated fibers lining such pores quickly become saturated with copper sulfide and depleted of cadmium sulfide and further removal of copper on that paper is no longer possible. A mottled spot results.

Figure 5 shows papers of this sort which were clamped together without a separator. The second paper receives high concentrations of copper where the solution streams through large pores of the first and the distribution of such pores is thus graphically reproduced. This experiment also emphasizes the desirability of using separators between papers to allow for redistribution of copper in the solution before it meets the next paper. Then, if there are minor nonuniformities or if such should develop, they will not affect the uniformity of the succeeding paper. Of course, if it is merely desired to recover the copper or other metal and not to estimate the spot density colorimetrically, uniformity is not so important and the separators may be dispensed with.

Under the conditions already discussed, recovery of copper is satisfactory in volumes ranging from 10 to 1000 cc. Table III shows 20 micrograms of copper recovered from volumes of 10, 100, and 1000 cc. The intensities of the resulting spots are identical within the limits of photographic reproduction.

TABLE IV. RELATION OF CONCENTRATION OF COPPER TO DENSITY OF SPOT

(Volume, 250 cc. Rate of flow, 2 cc. per minute per sq. cm. 0.01 molar H₂SO₄, buffered with 0.1 molar sodium acetate)



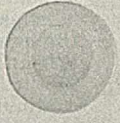

















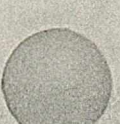
No.	Copper γ	Diameter of Flange Cm.	Area Ratio	Spot
1	22.5	1.5	9	
2	10	1.0	4	
3	2.5	0.5	1	
4	5	1.5	9	
5	5	1.0	4	
6	5	0.5	1	

That a given quantity of copper per unit area of exposed paper produces a spot of given density is shown in Table IV. The flanges used were 5, 10, and 15 mm., respectively, in diameter and the areas of the papers were consequently in the ratio 1 to 4 to 9, the ratio which was used for the concentrations of the three copper solutions—10, 40, and 90 micrograms in 250 cc. in tests 1, 2, and 3. These spots show the same densities. In tests 4, 5, and 6 the copper concentration was held constant, thus producing spots whose densities are inversely proportional to the areas.

Control of the flange size thus provides a device by which the sensitivity of the test may be regulated within practicable limits. A half microgram of copper is easily visible on a 1-sq. cm. area. By reduction of this area to 0.1 sq. cm., 0.05 microgram would be equally easy to detect. Further, estimation of quantity need not necessarily be made by comparison of spots of the same area, so long as the areas are known.

In Table V is reproduced a series of spots showing the recovery of varying quantities of copper between 1 and 100 micrograms from 500 cc. of solution on exposed areas 1 cm. in diameter. In these and other experiments cited in this part of the article, the excess cadmium sulfide was removed from the disk containing the copper spot immediately after

TABLE V. COPPER REMOVAL ON CADMIUM SULFIDE PAPER
(500 cc. of 0.01 molar H_2SO_4 , buffered with 50 cc. of molar sodium acetate passed at 1 cc. per minute per sq. cm.)

No.	Copper		Cadmium Sulfide Disk		
	Added γ	Concentration P. p. m.	First	Second	Third
1	100	0.20			
2	50	0.10			
3	25	0.05			
4	10	0.02			
5	5	0.01			
6	2	0.004			
7	1	0.002			

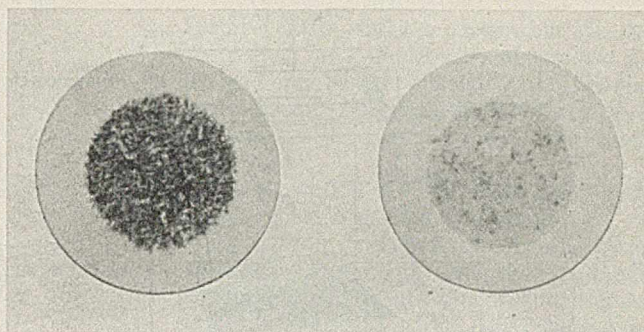


FIGURE 5. MOTTLED SPOTS ($\times 2$)

Showing effects of too heavy impregnation combined with absence of separator between successive disks.

Liquid flow is thus restricted to the larger pores of the first paper because smaller ones are clogged. The second disk was too close to the first to allow a redistribution of the solute leaving it; hence it has reproduced the pore pattern of the first.

the solution had percolated through it. Removal is effected by repeated immersion in warm 1 molar hydrochloric acid, the excess acid being blotted off between immersions. The disk is then thoroughly washed in distilled water. If the spot is allowed to remain wet for long periods with the cadmium sulfide unremoved, a tendency towards conversion of the green-black copper sulfide to a brown-colored product has been noticed. Removal of excess impregnant with molar acid then fails to restore the original color of the spot and on treatment with 10 per cent potassium cyanide, which dissolves the copper sulfide, yellow spots of cadmium sulfide remain in the area which it occupied. Some of the cadmium sulfide apparently is rendered insoluble through prolonged association with the copper sulfide, possibly through formation of a double compound.

From Table V the following conclusions seem admissible:

1. Recovery on three disks is practically complete for quantities up to 50 micrograms. The 100-microgram series shows a spot density on the third paper corresponding approximately to 1 microgram. Hence we may assume that the quantity which passed unprecipitated was less than 1 microgram or 1 per cent of the whole. It seems, however, somewhat risky to trust recovery of this quantity to three papers using this area.

2. The quantity detectable is less than 1 microgram in 500 cc. Actually a spot on a 1-cm. flange opening was obtained with 0.5 microgram but because of uncertainty of photographic reproducibility this was not included. This corresponds, therefore, to one part per billion.

3. The range over which estimations may be made safely by comparison of spot densities is not altogether evident from the photographs shown. When the copper sulfide is deposited only in the fiber layers near the surface, into which incident light penetrates, density comparisons may be satisfactorily made with surface illumination—that by which the photographs were taken. Thus, up to 10 micrograms the gradation is readily seen. When the penetrable surface layers have reached their saturation point, however, further increase in spot density is observable only by transmitted light and hence the heavier spots do not show a significant difference here, although against an illuminated background of suitable intensity the gradation is still observable up to 50 micrograms.

Such a background is conveniently provided by the illuminator shown in Figure 6. This consists of a glass-topped box containing a tubular incandescent bulb, a diffusion screen above which is a slot for

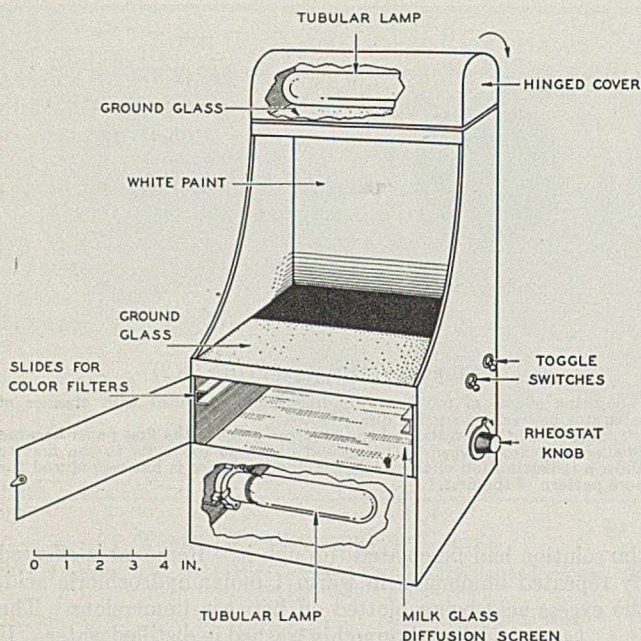


FIGURE 6. ILLUMINATING STAND FOR COMPARISON OF SPOTS

The stand is equipped to supply either incident or transmitted light. The latter is controllable by means of a rheostat and color filters.

insertion of color filter plates, and a rheostat for controlling the light intensity. A reproducible source of incident light is also included. The details are evident in the sketch. For the copper sulfide spots, a light yellow filter has been found to facilitate matching. In general, the range over which the matching is most accurate is from 0.5 to 10 micrograms per sq. cm.

TABLE VI. RECOVERY^a OF COPPER ON CADMIUM SULFIDE PAPER

No.	Cu Taken γ	Cu Recovered ^b γ
1	20	19
2	20	19
3	20	21
4	20	20
5	50	48
6	50	49

^a Conditions of Recovery:

Volume Solution	500 cc. 0.01 molar H ₂ SO ₄ + 0.1 molar NaAc
Rate of flow	1 cc. per minute per sq. cm.
Area of spot	0.8 sq. cm.
Number of papers, each separation	3

^b Readings on standard solutions were reproducible to $\pm 1\%$.

The sensitivity of cadmium sulfide paper for silver was found to be considerably greater than for copper. In a liter 0.2 microgram is still easily detectable on a 1-sq. cm. spot. The sensitivity for this area thus reaches one part in five billion.

The final proof of the completeness of recovery rests on the determination, by an independent method, of known quantities added to solutions and thus separated. To this end, spots from 500-cc. solutions containing 20 and 50 micrograms of copper were digested with nitric-sulfuric acid mixture, the excess was removed by evaporation, and the residue was dissolved in 2 per cent ammonium citrate. The solution was transferred to a small separatory funnel and to it were added 5 cc. of 1 per cent sodium diethyldithiocarbamate and 5 cc. of 1 to 1 ammonia. The brown copper diethyldithiocarbamate was then extracted with three portions of 5, 3, and 2 cc., respectively, of amyl alcohol. The extracts were

compared with standards in the Leitz universal colorimeter. The results are shown in Table VI.

Applications

The primary purpose of this article is to present a general technic for the separation of traces, adaptation of which may be made to specific analytical problems. Nevertheless it seems desirable to conclude with a few briefly stated examples, illustrative of such adaptation.

SEPARATION OF COPPER FROM NICKEL. Buffered solutions of "pure" nickel containing up to 10 grams per liter of the metal can be passed through cadmium sulfide paper without affecting it, and from such solutions traces of copper are recoverable with the same ease as from a water solution containing the same quantity of copper alone. A few micrograms of copper in samples of nickel ranging in weight from a fraction of a gram to several grams may be separated and estimated, either from the density of the copper sulfide spot obtained or by colorimetric or titrimetric methods applied to the ashed paper. A convenient and rapid method is thus provided for the estimation of copper in commercial nickel or in nickel electroplating baths. The copper content may be estimated when as low as 0.0001 per cent.

PROCEDURE. Based on the copper expected, dissolve in 1 to 1 nitric acid a quantity of sample sufficient to provide 10 to 30 micrograms of copper. Evaporate off the excess acid, add perchloric acid, and fume to a moist residue. Dilute, adding 100 cc. of 0.1 molar sodium acetate for each gram of nickel present. Test the reaction with Congo Red paper. If still acid, add sodium acetate in concentrated solution, until the reaction is alkaline. Pass this solution, at 1 cc. per minute per sq. cm., through three cadmium sulfide disks in a 1-cm. flange assembly. When the nickel solution reaches the bore of stopcock *C* (Figure 2), turn this to admit a wash solution of 0.1 molar sodium acetate, continuing the flow until the liquid drains colorless. Remove the disks and transfer each to a micro-Büchner funnel for treatment to remove the excess cadmium sulfide.

A convenient assembly containing a number of these funnels with separate receivers is shown in Figure 7. (Such an arrangement is particularly useful where several successive treatments of the paper are necessary.) First place a disk of blotting paper on the perforated funnel bottom in order better to distribute the suction. Wash with warm 1.5 molar hydrochloric acid saturated with hydrogen sulfide until the yellow color of the cadmium sulfide is completely removed. Then wash with water until the paper no longer reacts acid. Remove and dry. If the quantity of sample was properly chosen, practically all the copper will have separated on the first disk and it may be estimated by comparison with standard spots.

TABLE VII. COPPER DETERMINATION IN "PURE" NICKEL

	Weight of Sample Grams	Time Required Total running time		Copper Found %
		Man-hours	Hours	
Macromethod ^a	10	3	10	0.0075 \pm 0.0005
Micromethod				
Spot density	0.1	0.5	1.5	0.008 \pm 0.002
Iodometric	0.1	1	1.75	0.0085 \pm 0.0005

^a Separation as sulfide with H₂S; iodometric titration.

More precise determination can be made on the ashed spot. To avoid appreciable loss of copper, ashing requires careful control of the heating. Since this is not easily accomplished with a gas flame, the authors use the electrically heated crucible furnace shown in Figure 8.

Tall-form 2-cc. porcelain crucibles are used when ashing is combined with acid treatment. The winding, of platinum-rhodium alloy, conforms in shape to the crucible and is heated by a current supplied at 6 to 8 volts from a step-down transformer. Since it is only superficially imbedded in the Alundum furnace wall, the temperature lag is greatly reduced, making

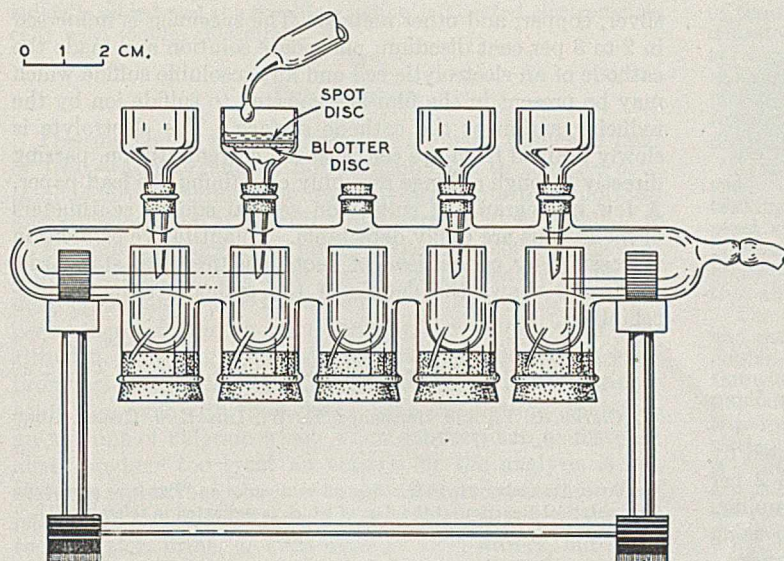


FIGURE 7. ASSEMBLY FOR TREATING SPOTS WITH LIQUID REAGENTS

possible an almost instantaneous heat control by means of a suitable rheostat.

The excess paper is trimmed away from the spot, which is then folded to a small pellet without touching the front surface and placed in the crucible, and the volatile matter is carefully distilled off without ignition. The crucible is cooled and a small drop of concentrated sulfuric acid is run down the wall to wet the carbonaceous mass. The acid is cautiously evaporated, after which the temperature is raised until a red glow in the residue indicates ignition of the carbon. The furnace heat is then cut off. When the residue no longer glows, another drop of acid is added, it is evaporated, and the temperature is raised to a barely perceptible redness (550° to 600° C.) to complete burning of the carbon. Under no circumstances should the temperature be allowed to reach the decomposition point of copper sulfate (650° C.).

To the residue in the crucible is added 0.05 cc. of glacial acetic acid, followed by warming for 1 to 2 minutes on a steam bath. A half cubic centimeter of water is then added, together with a small fragment of potassium iodide and a drop of starch solution. The liberated iodine is titrated with 0.001 *N* thiosulfate, added from a microburet graduated in 0.001-cc. divisions. A suitable stirrer may be made from platinum wire by fusing a bead at one end and beating this flat.

With proper equipment available, the whole procedure of ashing and titrating can be carried out in less than 15 minutes.

In devising other methods for estimation of the copper it should be remembered that the spot is contaminated with traces of cadmium sulfide which have escaped removal by the hydrochloric acid treatment.

Table VII presents data illustrating the time-saving feature of the proposed method. The precisions indicated, as well as the times, are to be taken only as approximations, since only one determination was made by each method.

COPPER IN LEAD. By a method similar to that just described for nickel, copper may be separated, along with most of the bismuth, from lead, thus facilitating its rapid estimation. From 0.1 to 1 gram of the sample is dissolved in nitric acid, and the solution is buffered and percolated through cadmium sulfide disks.

Lead separates with the copper, but this does not reduce the completeness of removal and the lead may be later dissolved out of the spot, together with the excess cadmium sulfide, by treatment with warm 1.5 molar hydrochloric acid.

The separation of silver from lead by this method is being studied by the authors.

ESTIMATION OF TRACES OF LEAD IN WATER AND AIR. From neutral solutions containing not too high a concentration of salts, lead may be removed on zinc sulfide paper with a sensitivity approximating that of the copper removal. Zinc and lead sulfides approach each other in solubility much more closely, however, and the reaction is therefore more susceptible to interferences than are those with copper, bismuth, or silver. Acetates in particular must be absent. The solution cannot contain high concentrations of such salts as nitrates and chlorides. Further, fixation of lead sulfide from solutions whose pH is above 8 is poor, the product being easily washed out of the disk because of its colloidal condition.

For the estimation of lead in drinking water, however, the method may have possibilities, particularly for field use, since nothing but the flange assembly and paper is required, estimation being made by spot-density comparison with standards. Copper sulfide may be removed from the spot

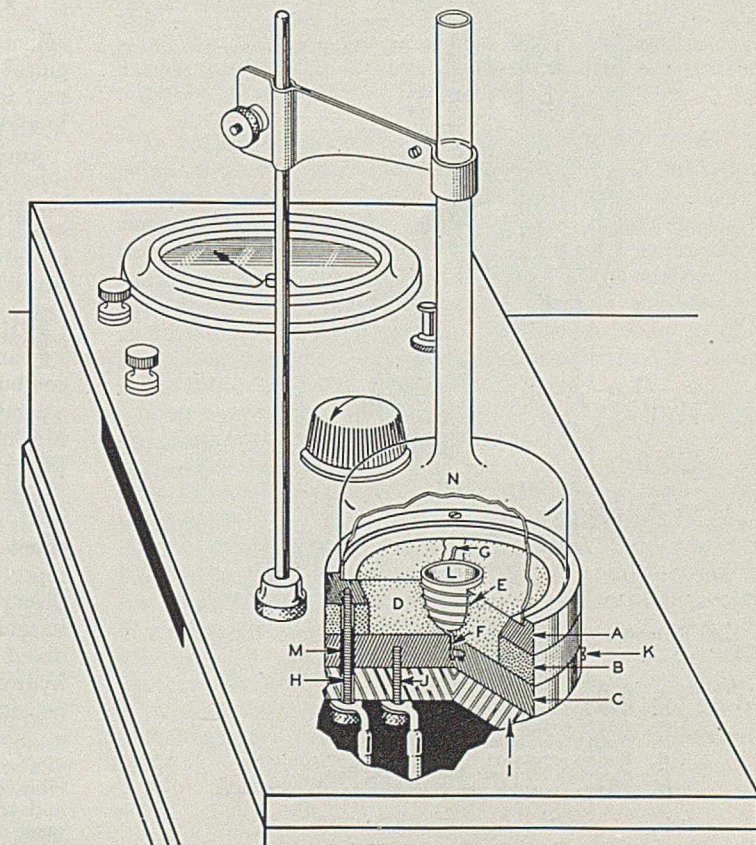


FIGURE 8. CRUCIBLE FURNACE MICROASSEMBLY

Ring A and plate C, of Duralumin, and separating ring B, of Transite, comprise the furnace body, mounted on Transite panel I. A and C are insulated from each other by B and glass bushings M and carry current to winding E, which is fastened at F and G. Current to the furnace is supplied through mounting screws H, to the top ring, and J, to the bottom plate. Space D is filled with Alundum cement, in which is molded the depression for crucible L. A glass bell protects the contents of the crucible from dust and drafts.

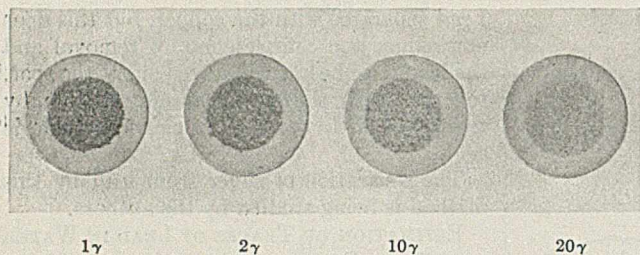


FIGURE 9. LEAD SPOTS ON ZINC SULFIDE PAPER

Lead removed from 250 cc. of water

without affecting the lead sulfide by treatment with 5 per cent potassium cyanide.

Likewise the estimation of lead in air might be effected by the use of a suitable water impinger containing 1 to 2 per cent of nitric acid. At the completion of the air sampling, the solution is neutralized with potassium hydroxide, using methyl orange, and passed through the zinc sulfide paper.

Figure 9 shows spots obtained with neutral lead solutions through zinc sulfide paper.

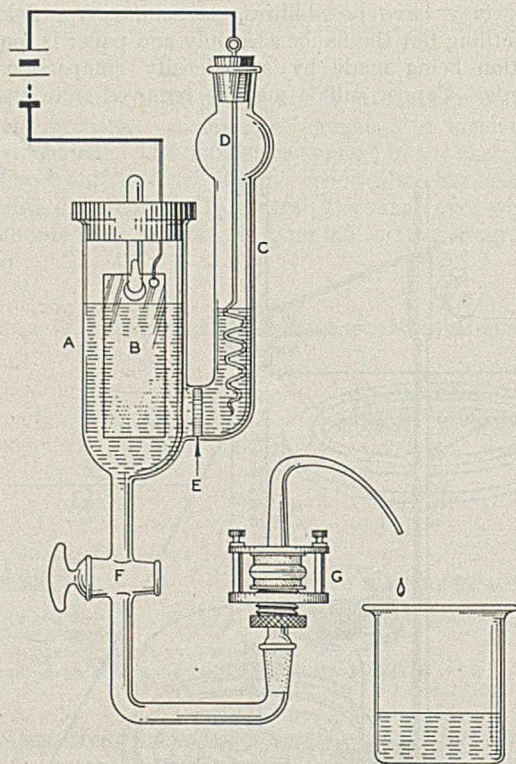


FIGURE 10. APPARATUS FOR CATHODIC REDUCTION OF TARNISH FILMS

- A. Cathode chamber
- B. Specimen (cathode)
- C. Anode chamber
- D. Anode (platinum spiral)
- E. Porous separator
- F. Stopcock for controlling rate of flow
- G. Flange assembly containing lead carbonate disks

DETECTION AND ESTIMATION OF SULFIDE IN TARNISH FILMS. Lead carbonate or phosphate paper can be used to remove sulfide ion, provided the solubility of the impregnant is reduced by an excess of phosphate ion and the pH is held between 7 and 8. This has furnished the basis of a convenient method for the detection of sulfide in thin tarnish films on

silver, copper, and other metals. The specimen is immersed in 2 to 3 per cent disodium phosphate solution and made the cathode of an electrolytic cell and any insoluble sulfide which may be present in the film is converted to sulfide ion by the reducing action at the cathode surface. The electrolyte is slowly drained from the cell with the current still on, passing directly through a flange assembly containing the lead paper. A few micrograms of sulfide on several square centimeters of metal thus are easily detectable. Quantitative estimation is possible by comparison of spot densities with standards. Figure 10 shows the details of the cathodic reduction assembly.

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- (1) Clarke, B. L., and Hermance, H. W., *IND. ENG. CHEM., Anal. Ed.*, 9, 292 (1937).

RECEIVED December 21, 1937. Second in a series on "Paper as a Medium for Analytical Reactions," the first of which is indicated in reference (1).

Determination of Iodine In Drinking Water, Urine, and Substances Containing Only About 1000 Times as Much Organic Matter as Iodine

A. C. BRATTON AND J. F. MCCLENDON, WITH THE TECHNICAL ASSISTANCE OF WILLIAM FOSTER AND RALPH WHITE

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THE senior author has been engaged in iodine micro-analysis since 1922 (7) and was the first to make closed combustions on biological materials, both in a bomb (6) and a combustion tube (silica, 5). His method was improved by McClendon and Remington (9) and McClendon and Bratton (8).

Open ashing involves losses. Wet combustion has been used, but usually the reagents are about one hundred million times the weight of the iodine to be analyzed. In the work reported in the present paper the quantities of reagents have been reduced to a minimum—in fact, the only reagents added in more than milligram quantities are sulfuric acid, of which about 2 cc. are used (diluted to 3 cc. with water), and sodium hydroxide, of which less than a gram is usually all that is necessary.

The material is fused with sodium hydroxide in a nickel crucible, dissolved in water with a few milligrams of sodium azide, and transferred to a microstill (8, Figure 4). After boiling off most of the water in the still, and adding the acid, a little ferric iron, and 2 cc. of bromine water, the material is placed in a receiver. The iodine is now driven over with the rest of the water by flaming the trap as far as the cold part of the condenser. It is necessary to distill some of this sulfuric acid in order to recover all the iodine, because of the presence of traces of reducing substances (destroyed by 4 minutes' boiling of the sulfuric acid). The bromine in the receiver oxidizes the iodine to iodate. The excess iodate is removed by boiling and aeration. Potassium

iodide is added and the resulting iodine is titrated electrometrically with sodium thiosulfate.

Procedure

This method is not applicable to ordinary tissues of land or fresh-water organisms but is applicable to samples containing only milligram quantities of organic matter, chlorides, and silicates, and at least 0.2 microgram (γ) of iodine. It is, therefore, applicable to nearly all organic compounds containing iodine, as well as to thyroid gland, seaweed, sponge, gorgonians, and other tissues which contain relatively high percentages of organic compounds with iodine in their constitution. Although moderate amounts of chlorides or even bromides do not interfere, hydrochloric and hydrobromic acids pass over with the iodine during distillation; therefore an amount of chloride which when converted to acid would alone produce too great an acidity for the analysis is not allowed, and in fact, the sample should not contain more than half a millimole of chloride. The method is not applicable to sea water, brine, or even some mineral waters, but since the chlorides of drinking water are usually low, it is possible to analyze the iodine in less than 1 liter of drinking water.

The method is not applicable to soil samples because of their high silicate content, but soil solution may be analyzed (as drinking water), provided the chloride content is not over 0.5 millimole. Where larger quantities of alkali are used in fusion of the sample, or where water contains considerable alkali, more sulfuric acid must be used in the still.

Thyroid gland or marine animal or plant tissues are fused with alkali and a trace of rare earth oxide (as an oxidation catalyst) and transferred to the still with a few cubic centimeters of azide solution and double-distilled water.

Five cubic centimeters of urine containing 0.2 γ of iodine may be analyzed, after destruction of the urea by fusing with 1 gram of sodium hydroxide and 2 mg. of mixed rare earth oxide (as an oxidation catalyst) until the last bubbles of ammonia are distilled off.

Whereas natural water samples are made alkaline by adding sodium hydroxide and azide (as a rule, 10 to 20 mg. of azide per liter are sufficient to destroy nitrite that would cause loss of iodine during evaporation), and then evaporated to dryness and fused with a trace of rare earth oxide before introduction into the still, chlorinated water is evaporated and fused before adding the azide, which not only destroys nitrite but reduces iodate.

DISTILLATION. The still used (8, Figure 4) is made of a 100-cc. round-bottomed, long-necked Pyrex flask with side neck close to the top. An inverted funnel is inserted in the neck as a trap to prevent the introduction of iron into the distillate in the form of spray (which would cause the results to be high). A hole is blown in the stem of the funnel and the tip is closed and sealed to the mouth of the flask, which is closed by fusion. A condenser is sealed to the side neck.

Any silica gel left in the still from the last distillation is dissolved out with sodium hydroxide. The air inlet of the still is connected with the compressed air supply, which introduces about one bubble a second. The condenser is connected with running water and the solution is evaporated in the still to about 3 cc. in volume. A 10-cc. test tube containing about 2 cc. of bromine water is placed as a receiver, 3 cc. of 21 *N* sulfuric acid are introduced through the air inlet, followed by 0.2 cc. of 4 per cent ferric sulfate solution, and the air stream is continued. As the solution is evaporated, if chlorides are present in the sample, hydrochloric acid will distill over.

When fumes of sulfur trioxide appear in the still, the gas flame of the microburner is reduced to 5 mm. and distillation is continued for 2 minutes. After about 1 minute of this period the trap in the neck of the distilling flask is heated with a large flame until all the moisture has disappeared. Since the water seal of the trap is evaporated and therefore the trap is not now functioning in the normal manner, the still must be carefully watched for 4 minutes; no spray should be allowed to pass into the condensing tube, as any iron in the distillate will destroy the accuracy

of the results. At the end of the 4 minutes of fuming, the condenser outlet is washed with a little water and the receiving tube is removed.

EVAPORATION OF EXCESS BROMINE. The receiving tube is placed in a boiling water bath and air is bubbled through a capillary lowered into it until the bromine is evaporated (color disappears) and for 10 minutes longer, then cooled in melting ice.

TITRATION. A 1-cc. buret (4) graduated in thousandths is used. The volume between the stopcock and the tip of the braking capillary at the top should be small, and the tip of the pipet should be well constricted in a long capillary (to be immersed). The receiving tube is clamped to a ring stand and a high-speed stirrer is inserted which must not rotate so rapidly that air is entrained.

The concentration cell, which consists of one electrode inside and one outside a pipet (Figure 7, 8), is connected by a single-pole double-throw switch to a 1- to 10-microfarad condenser, and by throwing the switch to the opposite position, the condenser is discharged through a moving-coil galvanometer, whose deflection is proportional to the charge on the condenser and hence to the electromotive force of the concentration cell. The galvanometer is short-circuited by the critical damping resistance. Ten milligrams of dry or freshly dissolved potassium iodide are added to the receiving tube that serves as a titration vessel and the pipet electrode is inserted.

The iodine solution is drawn up into the pipet electrode by means of a rubber bulb about ten times to make sure that the same concentration prevails inside as outside, and this is verified by noting the zero potential. The level inside the cell should always be above the point of the sealing of the platinum wire.

The microburet is filled with 0.001 *N* thiosulfate solution by suction, the capillary is adjusted at the top, the level is brought down to zero, and the tip is carefully washed off before inserting it into the 10-cc. receiving tube which serves as the titration vessel. Then 0.005 cc. of thiosulfate is introduced, the switch is thrown to charge the condenser and after 15 seconds is thrown to the galvanometer, and the deflection is read. Then the pipet is rinsed again, but in this case a standard number of rinsings is sufficient without verifying the zero potential, and the process is repeated. After the galvanometer deflection reaches a maximum, 2 more titration increments are made on the down grade, the results are plotted, and the end point is found by connecting the points of reading. Immediately after the titration a standard containing 0.5 γ of iodine as iodate is titrated.

In both these titrations the "potassium iodide blank" in cubic centimeters of thiosulfate is subtracted and the iodine is calculated in the unknown. A "reagent blank" is also run every time any reagents are made up—i. e., distillation is made with the same amount of alkali, rare earth oxide, azide, sulfuric acid, and ferric sulfate as is used in the analysis and with the same amount of bromine water in the receiver. From the resulting titration the "potassium iodide blank," in cubic centimeters of thiosulfate, is subtracted and the iodine in the other "reagents" is calculated.

ACCURACY OR SENSITIVITY OF THE TITRATION. Close to the end point of the titration the addition of 0.001 cc. of 0.001 *N* thiosulfate will cause a deflection of many millimeters on the scale of a sensitive galvanometer. Since one division of the buret (0.001 cc.) of 0.001 *N* thiosulfate is equivalent to about 0.02 γ of iodate iodine (or the iodine liberated by the action of 0.02 γ of iodate iodine on excess iodide) and only 2 points on the titration curve before the end point are necessary, 0.04 γ of iodate iodine may be titrated. The authors have found 0.01 to 0.02 γ of iodate iodine in 10 mg. of the purest American and British potassium iodide which they have obtained even after recrystallization. Therefore they have not tried to increase the sensitivity by further dilution of the thiosulfate.

Reagents

DISTILLED WATER. All water used should be distilled, made alkaline, and redistilled in a nonmetal still for metals act as oxidation catalysts.

STANDARD POTASSIUM IODATE, 1.7835 grams of the recrystallized salt, dried 1 hour at 130° C., dissolved to make 1 liter of solution. This contains about 1058 γ of iodine per cc. It should be diluted to a thousand volumes.

POTASSIUM IODIDE. A solution of the recrystallized salt containing 10 mg. per cc. is made up just before using and 1 cc. is added to each titration. A blank may be run on 8 or 10 cc. One cubic centimeter should not contain more than 0.02 γ of iodate iodine.

STANDARD POTASSIUM IODIDE, 1.308 grams of the recrystallized salt (dried at 110° C.) per liter. One cubic centimeter of this diluted to 1 liter contains 1 γ of iodine per cc.

STANDARD 0.1 N SODIUM THIOSULFATE, 24.85 grams of the pure crystalline salt and 0.1 gram of sodium carbonate dissolved to make 1 liter of solution. It should be diluted to 0.001 N before use, adding 0.1 gram of sodium carbonate per 100 cc. of diluted solution in a paraffin-lined flask.

0.1 N SULFURIC ACID, 0.25 cc. of the pure concentrated acid diluted to 90 cc.

21 N SULFURIC ACID, 140 cc. of concentrated acid per 240 cc. of solution.

BROMINE. The purest bromine available is purified by washing 3 times with water (iodine goes in water as iodate). Bromine water is prepared by bubbling the bromine vapor through water just before use. One cubic centimeter of bromine water plus 5 cc. of 0.1 N sulfuric acid made up to 9 cc. is about the color of 0.07 per cent dichromate solution and is aerated 30 minutes at 100° C. It should not titrate more than 0.05 γ of iodate iodine.

FOUR PER CENT FERRIC SULFATE. Four grams of crystalline, hydrated ferric chloride are dissolved in 100 cc. of water plus 3 cc. of 6 N sulfuric acid. The solution is evaporated nearly to dryness over a free flame, 100 cc. of water are added, and the operation is repeated. Upon dilution to 100 cc., the solution is filtered if necessary.

SODIUM AZIDE (Eastman's or Kahlbaum's), 500 mg. in 100 cc. of water.

0.1 N SODIUM HYDROXIDE, 0.4 gram of (c. p.) sodium hydroxide per 100 cc. of solution, in a paraffin-lined bottle. Since it usually contains some carbonate, it is preferably dissolved in an equal weight of water and the carbonate is settled, then it is diluted and titrated with standard acid. It is used in cleaning the electrodes and still and in determining the acidity of the solutions in which iodine is determined.

RARE EARTH OXIDE, mixed oxides of lanthanum, cerium, neodymium, praseodymium, and samarium. Since it is difficult to separate these oxides, they are used in this impure form as oxidation catalysts.

Experimental

Iodine may be concentrated and removed from interfering electrolytes by precipitation as silver or palladium iodide, by extraction of iodide from carbonate solutions with 93 per cent ethyl alcohol, or by extraction of iodine with carbon tetrachloride, but these methods are either inapplicable to 1 γ quantities of iodine or unduly time-consuming. Therefore distillation (which had been used by McCullagh and by Leipert) was developed as a micromethod accurate for small quantities (0.2 to 10 γ) of the element.

An attempt to receive iodine vapor in sodium hydroxide plus hydrogen peroxide failed, since hydrogen peroxide cannot be completely destroyed, even by baking the evaporated solution. It may be removed in acid solution, but boiling the acid solution resulted in loss of iodine as hydrogen iodide. In one experiment, hydriodic acid in 8 cc. of water plus 0.625 cc. of 0.1 N sulfuric acid was aerated 10 minutes at 100° C. The loss was 15 to 20 per cent.

TABLE I. MINIMUM QUANTITY OF SODIUM SULFITE TO REDUCE 1 γ OF IODATE IODINE

0.2% Na ₂ SO ₃ Cc.	5% NaOH Cc.	6 N H ₂ SO ₄ Cc.	6% Hydrated Ferric Ammonium Sulfate Cc.	Recovery of Iodine in Receiver %
0.1	1	5	0.5	90.3
0.5	1	5	0.5	99.0
1.0	1	5	0.5	96.4

The iodine might be received in sodium hydroxide, but the blank is augmented by the reagent. It was found most satisfactory to receive the distilled iodine directly in bromine water. No iodine was lost even with the delivery tube at

some distance from the surface of the bromine water, but to be safe, the tip of the condenser was kept just above the level of the oxidant. Steam-distillation of iodine was not nearly as quantitative as air-distillation.

Nitrous acid is a fairly good oxidizer for iodine and possesses the added advantage that it will reduce any hypiodite or iodate, but it is not dependable for 1 γ quantities. In fact, it was found necessary to destroy traces of nitrous acid (formed in the alkali fusion of the material) with sodium azide before oxidation of the iodide to iodine.

Obviously, the alkaline solution in the still must be concentrated to small volume before acidification, so as not to overflow the receiver with the distillate. The excess hydrazoic acid may be conveniently removed from the solution by boiling after adding the acid to the still. Ferric iron was found to be the best oxidant for liberating iodine, catching the distillate in bromine water to prevent loss of iodine as hydriodic acid.

Minimal quantities of reagents must be used not only to reduce the blank but to increase the efficiency of removal of iodine. Table I shows the minimum quantity of reducing agent necessary to reduce iodate before the solution is transferred to the still. In this case sulfite was used, but similar results were obtained with azide.

TABLE II. QUANTITY OF ACID USED IN DISTILLATION

(Still charge consisted of 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, 1 cc. of 0.5 per cent sodium hydroxide, 0.2 cc. of 4 per cent ferric sulfate, and 1.1 γ of iodine as iodide.)

6 N H ₂ SO ₄ Cc.	Recovery of Iodine in Receiver %	Mean %
0.5	50.8	45.8
0.5	40.8	
1.0	64.0	70.4
1.0	76.8	
2.0	66.5	79.7
2.0	99.7	
2.0	59.5	
2.0	93.0	
3.0	89.0	91.5
3.0	93.9	
4.0	88.2	85.6
4.0	82.9	

The data in Table I indicate that 0.5 cc. of 0.2 per cent sodium sulfite is ample to reduce 1 γ of iodine from iodate to iodide (but this did not reduce all the nitrite), and Table II indicates the optimum amount of 6 N sulfuric acid to be about 3 cc. (After fusion, more acid must be used to neutralize the sodium hydroxide, and 21 N is preferable.)

Ferric sulfate is as efficient as ferric ammonium sulfate as an oxidant (Table III), and is preferable because less electrolyte is introduced. Table III indicates that 0.2 to 0.4 cc. of 4 per cent ferric sulfate should be used.

The volume of water introduced with the acid is important; 6 N sulfuric acid is superior to 3 N, as shown in Table IV.

Finally, the method of distillation is of extreme importance. Some iodine is held by the water which condenses in the trap; this iodine cannot be effectively driven over by adding more water to the still and evaporating nearly to dryness (sulfur trioxide fumes), repeating the process several times, as was done in obtaining the data for Tables I, II, and III. Even with optimum quantities of reagents, the loss still amounts to 5 to 10 per cent. If, however, the trap be heated to prevent condensation at the end of the distillation, the maximum loss of iodine amounts to only 3 per cent (Table V) on inorganic solutions. In the presence of traces of organic matter, however, iodine continued to come over 3 minutes after the appearance of sulfur trioxide fumes with a 5-mm. flame (destroying traces of organic reducing substances by micro-Kjeldahl technic).

TABLE III. COMPARISON OF FERRIC SULFATE WITH FERRIC AMMONIUM SULFATE AS OXIDIZING AGENT

(Still charge consisted of 1.1 γ of iodine as iodide, 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, 1 cc. of 0.5 per cent sodium hydroxide, and 2 cc. 6 N sulfuric acid.)

Oxidant Cc.	Recovery of Iodine in Receiver	
	6.6% ferric ammonium sulfate (hydrated) %	4% ferric sulfate %
0.2	92.5	99.7
0.2	..	66.5
0.2	86.7	93.0
0.2	..	59.5
	Mean 89.6	79.7
0.4	83.5	85.5
0.4	..	85.5
	Mean 83.5	85.5
0.7	84.7	78.0
0.7	84.4	77.2
	Mean 84.6	77.6
1.0	85.0	..
1.0	74.2	75.5
	Mean 79.6	75.5

OXIDATION OF IODINE TO IODATE BY BROMINE, AND REMOVAL OF EXCESS OXIDANT. One-half cubic centimeter of saturated bromine water is ample to oxidize 1 to 10 γ of iodine to iodate. The excess cannot be removed by treating with formic acid or phenol as in the macrooxidation, because of incompleteness of reaction between formic acid or phenol and bromine. An error of +2 per cent will be introduced in the 10 γ titration or +20 per cent in the 1 γ titration. Because of the reducing action of hydrazoic acid, 2 cc. of bromine water are used; if this bromine disappears during distillation more bromine water is added.

TABLE IV. DISTRIBUTION OF IODINE IN DISTILLATES

(Still charge consisted of 1.1 γ of iodine as iodide, 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, and 0.2 cc. of 4 per cent ferric sulfate at the proper time.)

Fraction of Distillate	Volume of Fraction Cc.	Total Iodine in Fraction, Acidified with:	
		6 cc. of 3 N H ₂ SO ₄ fraction	3 cc. of 6 N H ₂ SO ₄ fraction
		%	%
1st	2	15.0	54.1
2nd	2	48.3	37.0
3rd	2	25.3	8.9
4th	2	11.4	0.00

Iodic acid is perfectly stable at 100° C. for 30 minutes or more. Aeration of the acidified solution at 100° C. may therefore be used.

One-half microgram of iodine as iodate was put in each of 4 tubes, and to it were added 1, 5, 5, and 7.5 cc., respectively, of 0.1 N sulfuric acid. Tube II was used as standard and tubes I, III, and IV were made up to 9 cc. and aerated at 100° C. for 30 minutes. Tube I titrated 0.5 γ , tube III 0.5 γ , and tube IV 0.504 γ of iodine.

In order to determine the "bromine blank," 2 series of 4 titrations each were made on acidified bromine water alone. In the first series the total bromine added was constant, but the aeration of the first was so great as to break bubbles at the top of the tube, and the others progressively decreased. The titrations were 0.0045, 0.0048, 0.0045, and 0.005 cc. of thiosulfate. In the second series the aeration was constant, but the quantity of bromine water was 1/9, 2/9, 3/9, and 4/9 of the amount required to match 0.07 per cent potassium bichromate solution. The titers were 0.0044, 0.0042, 0.0045, and 0.0042 cc. of thiosulfate. If the aeration is not performed in a hood it is necessary to open the windows before titrating. The bromine blank is not due to iodine in the 0.1 N sulfuric acid, since a series of 3 brominated tubes with 1, 2, and 5 cc. of this acid titrated 0.004, 0.0045, and 0.0045 cc. of thiosulfate.

The presence of sodium sulfate retards the removal of bromine, so that it is not practical to receive the iodine in hypobromite and then add sulfuric acid.

MICROTITRATION OF IODINE. Small quantities of iodine may be determined gravimetrically by precipitation as silver

or palladium iodide, but this method is not sufficiently sensitive for 1 to 10 micrograms of the element. The titration of iodide ion with mercuric chlorate or with silver nitrate, using a silver-silver iodide electrode, also lacks sensitivity. Most schemes for the determination of 1 to 10 γ of iodine oxidize the element with bromine water to iodate by the Winkler technic, since six times the original quantity of iodine becomes available for titration upon addition of potassium iodide to the iodate. Sodium thiosulfate is the most useful reducing solution for the titration of the free iodine, but the use of starch as indicator for this determination introduces error, since an appreciable amount of iodine (at least 0.05 γ in 2 cc.) is required to give the final faint blue color to the starch. In this research an electrometric method has been modified for titration of the small volumes of solution encountered.

TABLE V. COMPARISON OF METHODS OF DISTILLATION

(Still charge consisted of 1.1 γ of iodine as iodide, 0.5 cc. of saturated sodium carbonate, 0.5 cc. of 0.2 per cent sodium sulfite, 1 cc. of 0.5 per cent sodium hydroxide, 3 cc. of 6 N sulfuric acid, and 0.2 cc. of 4 per cent ferric sulfate.)

Method	Error Per Cent of Total Iodine
Distill to sulfur trioxide fumes	
Flaming trap only at termination of distillation	-3.5
Flaming trap constantly during distillation	Av. 0.0, -2.8, +0.2, -2.4 -1.2

The dead-stop end-point method of Foulk and Bawden (1) was proved unsatisfactory. The differential method of MacInnes (10), using the pipet electrode of Hall, Jensen, and Bäckström (2) (but reduced to 0.1-cc. volume), gave satisfactory results, providing the electrode potential was used to charge the condenser and discharged through the galvanometer. The platinum wire must not be too small and must be heated to a white heat after bending into shape.

The titration solution should be vigorously stirred, but the entrainment of air is undesirable, since some iodide may be oxidized by it to iodine.

When more than 5 γ of iodine (as iodate) are to be titrated, the electrodes may be kept out of the solution until all but about 1 γ of the iodine has been reduced, otherwise the high iodine concentration may polarize the electrodes. Tenth-normal sodium hydroxide may be used to clean them even during the titration if the end point has not been approached, but the galvanometer deflections observed before cleaning the electrodes cannot be used in plotting the end point.

In titration of 1 γ of iodine as iodate, the volume of the solution should not be greater than 10 cc. As regards acidity of an iodine solution during thiosulfate titration, Kolthoff and Furman (8) give the following requirements:

	pH
0.1 N iodine	< 7.6
0.01 N iodine	< 6.5
0.001 N iodine	< 5

On plotting these pH values against concentration, we find in extrapolation to 0.000004 N solution a pH of around 2 is required. It was found empirically (Table VI) that a pH of 2.2 was most satisfactory. One cubic centimeter of 0.0625 N sulfuric acid added to make 10 cc. of final solution to be titrated will approximate this pH, but it is possible to titrate in the presence of 5 cc. of 0.1 N sulfuric acid. A potassium iodide solution containing 12.5 mg. per cc. was prepared, and 1 cc. of it was added to the acidified solution of iodate. The total volume of 10 cc. was determined by a mark on the tube. The completeness of the reduction of iodate depends both on the potassium iodide and acid concentration (Table VIII). For titration of 10 γ of iodine as

iodate, a 35-cc. volume was maintained for the solution to be titrated, and 2 cc. of the sulfuric acid and 2 cc. of the potassium iodide solution were added.

The buret used in titration was 0.1 cc., graduated in thousandths and with stopcock and air capillary at top, according to Lochte and Hoover (4).

TABLE VI. EFFECT OF ACID AND IODIDE CONCENTRATION ON TITRATION OF 1 γ IODINE AS IODATE

0.0625 N H ₂ SO ₄ Cc.	KI (12.5 mg. per cc.) Cc.	End Point Approximately 0.001 N Na ₂ S ₂ O ₃ Cc.	Type of Curve ^a
0.2	0.2	0.0574	Fair
0.2	0.6	0.0595	Good
0.2	1.0	0.0625	Good
0.2	1.4	0.0630	Excellent
0.6	0.2	0.0570	Good
0.6	0.6	0.0623	Good
0.6	1.0	0.0624	Good
0.6	1.4	0.0615	Excellent
1.0	0.2	0.0550	Poor
1.0	0.6	0.0600	Fair
1.0	1.0	0.0625	Good
1.0	1.4	0.0625	Excellent
1.4	0.2	0.0538	Poor
1.4	0.6	0.0555	Poor
1.4	1.0	0.0613	Good
1.4	1.4	0.0627	Excellent

^a A poor curve refers to a relatively flat one, where the inflection point cannot be conclusively established.

Thousandth-normal sodium thiosulfate is a convenient strength to use, since 1 γ of iodine as iodate requires about 0.005 cc., or about half the capacity of the buret. The sodium thiosulfate is prepared by dilution of 0.1 N solution. Table VII indicates the added stability afforded the dilute solution by addition of 0.1 gram of sodium carbonate per 100 cc. Nevertheless, it should always be standardized just before use or at intervals, and a time curve should be drawn.

TABLE VII. EFFECT OF ADDED SODIUM CARBONATE

Approximate Normality of Na ₂ S ₂ O ₃	Time Minutes	Fading %
0.0015	33	2.0 ?
	67	1.45
	309	4.35
	1860	13.1
0.001	30	3.3
	65	4.65
	305	6.0
	1860	6.8
0.0005	25	0.6
	61	1.2
	300	2.7
	1860	11.4
0.0005 + 0.1 gram of Na ₂ CO ₃ per 100 cc.	220	0.8
	1740	4.1

With such a small buret, the sodium thiosulfate cannot be added to the iodine solution fast enough to endanger precipitation of sulfur unless the acidity is very high, but it may be best to have the acidity of the standard equal to that of the unknown. Uniform increments should be added, for unequal increments near the end point necessitate an additional calculation. It was found that 0.005-cc. increments gave more reproducible results than 0.0025-cc. increments (Table VIII). In titration of very small quantities of iodine, smaller increments are imperative.

Since in some analyses hydrochloric acid (from chlorides) equivalent to about 3.5 cc. and sulfur trioxide equivalent to about 1.5 cc. of 0.1 N sulfuric acid are distilled, the effect of 5 cc. of 0.1 N sulfuric acid on the titration was studied and the type of curve was found to be excellent.

Eight rinses of the electrode pipet may be required before adding the next increment of the sodium thiosulfate, and

after adding the increment 15 seconds should elapse between throwing the switch to charge the condenser and reading the voltage.

The reproducibility of titration is 2 per cent (Table VIII).

The potassium iodide solution should be made fresh, as a sample that had stood 3 days increased its "iodate iodine" content from about 0.01 γ per cc. to 0.074 γ per cc. Since the total blank on all the reagents should not be more than about 0.08 γ , and 1 cc. of potassium iodide solution is used in an analysis, it is imperative to use fresh potassium iodide solution.

TABLE VIII. TITRATION OF 1 γ OF IODINE AS IODATE

0.005-Cc. Increments of Na ₂ S ₂ O ₃		0.0025-Cc. Increments of Na ₂ S ₂ O ₃	
End point Cc.	Variation from average	End point Cc.	Variation from average
0.0565	+0.7	0.0542	-2.3
0.0558	-0.5	0.0570	+2.7
0.0570	+1.6	0.0568	+2.3
0.0560	-0.2	0.0540	-2.7
0.0554	-1.3
Av. 0.0561		0.0555	

There are at least three sources of substances that might augment the amount of iodine in this analysis: the iodide in the reagents used, the bromine remaining after aeration, and the iodate iodine in the potassium iodide used in titration. Therefore a blank must be subtracted from the result.

Accuracy of the Method

Two hundred cubic centimeters of chlorinated tap water plus 0.1 gram (1 pellet) of sodium hydroxide were evaporated to a small volume, transferred to a nickel crucible, and evaporated to dryness, 0.5 gram of sodium hydroxide was added, and the material was fused. Water was added to dissolve the fusion and 2 mg. of sodium azide were added. This was transferred to the still and together with a similar sample to which 0.54 γ of iodine had been added, analyzed with an error of 2 per cent (Table IX). Two hundred cubic centimeters of deep-well water plus 0.1 gram of sodium hydroxide plus 2 mg. of sodium azide were evaporated to small volume and transferred to a nickel crucible, 0.5 gram of sodium hydroxide was added, and the material was fused, transferred to the still, and, together with a similar sample to which 0.55 γ had been added, analyzed with an error of 2 per cent (Table IX).

TABLE IX. ANALYSIS OF NATURAL AND CHLORINATED TAP WATER AND URINE

	Iodine in Sample γ	Iodine Added γ	Total Iodine γ	Differ- ence γ	Error %
200 cc. of Minneapolis tap water	0.43	0.54	0.98	0.55	2
200 cc. of LaGrange deep- well water	0.59	0.55	1.13	0.54	2
2.5 cc. of urine	0.975
5 cc. of urine	1.95	0.5	2.44	0.49	2

Urine (2.5 cc. plus 0.1 gram of sodium hydroxide plus 2 mg. of rare earth oxide) was evaporated in a nickel crucible to dryness; 0.9 gram of sodium hydroxide was added and fused; the material was dissolved in water, 2 mg. of sodium azide were added, and this, together with a similar sample of 5 cc. of the urine and a third sample of 5 cc. of the urine plus 0.5 γ of iodine, was analyzed with a recovery of 98 per cent (Table IX). The urine was from a person taking iodized salt.

Summary

After boiling the sample in alkaline solution (which hydrolyzes many compounds) and fusing with alkali with rare earth oxides as catalysts (which decomposes urea, evaporates ammonia, and begins the process of oxidation), the iodine may be freed by micro-Kjeldahl combustion in 4 minutes. Iodate is reduced and nitrite destroyed with azide. During the

micro-Kjeldahl combustion the iodide is oxidized to iodine by ferric iron and distilled into bromine water which oxidizes the iodine to nonvolatile iodate. The excess bromine is blown out with a current of air at 100° C. After adding 10 mg. of potassium iodide, the iodine is titrated with thiosulfate, using an electrometric method to determine the end point.

The method is applicable to drinking water, soil solution, urine, thyroid gland, seaweed, sponge, and many other substances, where a sample containing 0.2% of iodine contains only small quantities of organic matter (other than urea), silica, or halides.

The method may be used to titrate accurately 0.04 microgram of iodine, but a blank of about 0.02% must be subtracted on account of the potassium iodide. Blanks must be subtracted on account of the reagents used in the fusion, distillation, and bromination of the sample.

The electrometric titration is adapted to smaller quantities of iodine than heretofore. The distillation is performed with smaller additions of reagents than in previous methods. The method is shorter and less expensive than combustion tube methods.

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The Use of Trautz's Micro-Dumas Method with the Apparatus of Pregl

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A MICRO-DUMAS method has been described by Trautz in which the combustion products are swept out at the rate of four bubbles per second (1, 3, 4). This rate is more than four times that recommended by Pregl (2); the time required for a complete analysis is thus reduced to only a half hour. Trautz offered no analytical data other than an analysis of acetanilide, and carried out this analysis with apparatus in which the parts were connected by ground-glass joints.

TABLE I. TYPICAL RESULTS

	Nitrogen Found %	Nitrogen Calculated %
Azobenzene (C ₁₂ H ₁₀ N ₂)	15.32	15.38
p-Bromoacetanilide (C ₈ H ₈ OBrN)	6.65	6.58
2,4-Dinitrophenylhydrazine (C ₆ H ₆ O ₄ N ₂)	28.18	28.28
Phenylurea (C ₇ H ₈ O ₂ N ₂)	20.63	20.59
Theonine (C ₈ H ₈ O ₂ N)	11.71	11.76
N-Methyl-N,N'-diethyl-N-phenyltrimethylenediamine (C ₁₄ H ₂₄ N ₂)	12.72	12.72
tert-Butylglyoxal-2,4-dinitrophenylhydrazone (C ₁₂ H ₁₄ O ₄ N ₂)	19.19	19.05
Benzoylmethionine (C ₁₂ H ₁₆ O ₂ NS)	6.05	5.97
Flavone-2,4-dinitrophenylhydrazone (C ₂₁ H ₁₄ O ₅ N ₂)	13.85	13.91
5,5'-Methylallylethylmalonylurea (C ₁₀ H ₁₄ O ₂ N ₂)	13.40	13.33
Methylvaline (C ₆ H ₁₁ O ₂ N)	10.68	10.68
2-Phenyl-4-benzoylpyrrole (C ₁₇ H ₁₅ ON)	11.50	11.57
4,4'-bis-[N-(α,α'-dimethyl-β-carbethoxy)-pyrrole]-3,3'-dimethylbiphenyl (trans) (C ₂₂ H ₂₂ O ₄ N ₂)	5.32	5.46
Phenylhydrazone of tetramethoxygossypol (C ₁₄ H ₁₈ O ₄ N)	7.40	7.43
N,N'-[p,p'-[N-(2-hydroxy-1-propyl)-benzenesulfonamide]]-glutaramide (C ₂₂ H ₂₂ O ₅ N ₄ S ₂)	10.04	10.07
Sodium phenylsulfamate (C ₆ H ₅ O ₂ NNaS)	7.14	7.17

Experience in this laboratory has shown that it is possible to use this method with a slightly modified Pregl apparatus and that the method is applicable to a wide variety of compounds containing nitrogen. A complete analysis requires an average time of 30 minutes.

The following changes were made in Pregl's apparatus:

The tubing which joined the azotometer tip and the combustion tube tip, and the stopper at the end of the combustion tube were the only rubber connections used. The others were eliminated by sealing the joints together, in order to reduce the possibility of leakage.

A ball-and-socket ground-glass joint was made between the azotometer tip and the combustion tube tip. This was done by widening the former slightly, heating the latter in a flame until a thick wall was formed, and then grinding the two tips together with silicon carbide. A trace of vaseline was used in the joint. The tips were connected as usual with impregnated microtubing. The ground-glass joint was made to lessen the possibility of losing nitrogen at that point.

An electric furnace was used to maintain the permanent filling at 750° C. It was found that at this temperature no carbon monoxide passes through the combustion tube without being oxidized.

An asbestos tent was suspended over the wire gauze and moved forward with gauze and burner. The tent was used to facilitate a rapid and complete combustion.

Typical results from about 250 analyses are given in Table I (Pregl's 2 per cent correction was used throughout).

Acknowledgment

The author wishes to thank R. T. Milner for his interest and helpful suggestions.

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Relative Value of Certain Azo Derivatives of 8-Hydroxyquinoline as Analytical Reagents

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This paper continues a study begun by Gutzeit and Monnier, on the development of specific spot paper and spot plate analytical reagents, and reports the effect of eighteen azo derivatives of 8-hydroxyquinoline on nearly all the metals except the alkali, alkaline earth, and most of the rare earth metals.

Test reagents were saturated alcoholic solutions of the dyes, and test solutions contained 3 mg. of active constituent per ml. of 20 per cent nitric acid solution. In a few cases 20 per cent aqua regia and hydrochloric acid were employed.

The following derivatives of 8-hydroxyquinoline gave specific tests for the metals indicated: (I) 5-(2-hydroxyphenylazo)-,

Pd⁺⁺; (II) 5-(3-hydroxyphenylazo)-, Hg⁺⁺, Pd⁺⁺; (VI) 5-(2-chlorophenylazo)-, Pd⁺⁺; (VII) 5-(3-chlorophenylazo)-, Hg⁺⁺, Pd⁺⁺; (VIII) 5-(4-chlorophenylazo)-, Hg⁺⁺; (X) 5-(3-tolylazo)-, Hg⁺⁺, Pd; (XII) 5-(4-arsonophenylazo)-, Hg⁺⁺; (XV) 5-(8-hydroxy-3,6-disulfo-1-naphthylazo)-, Hg⁺⁺; (XVI) 5-(benzidinemonoazo)-, Pd⁺⁺, VO₂⁺, or VO₃⁻.

In practically all cases chloride ion obscures the test, but tartrate ion has, in general, no effect. This series of dyes does not give specific tests for copper, nickel, and molybdenum as MoOCl₅⁻ ion. Only a few dyes give specific tests for mercury and palladium which may be distinguished by the fact that hydrochloric acid destroys all tests for mercury.

A STUDY was made by Gutzeit and Monnier (2) of the effect of practically all the metals of the periodic table, except the alkali and the alkaline earth metals, on a series of sixteen azo derivatives containing the functional group 8-hydroxyquinoline. Consideration was given to the correlation of structure and specificity of the dyes. From their research, Gutzeit and Monnier have concluded that:

1. Except for a few minor and scattered reactions with various cations, the azo dyes containing the 8-hydroxyquinoline nucleus seem to give consistent reactions which are specific for mercury, copper, palladium, nickel, and molybdenum as MoOCl₅⁻.
2. The tests should be carried out in acid solution.
3. Certain anions such as tartrate and chloride obscure the results.
4. Polar groupings para to the point of coupling on the aromatic nucleus tend to increase the positiveness of the test.
5. A reagent with a given specific grouping, as the azo-8-hydroxyquinoline group, does not acquire new reactions with

new ions by substitution with different radicals, but the sensitivity and specificity of a given reagent can be improved by introducing other substituents without modifying the reactions of the functional group.

Some new azo derivatives of 8-hydroxyquinoline were prepared by Bennett and Shreve (1). The relative value of these dyes as analytical reagents was studied.

Experimental

Because of the low solubility of the dyes in the common solvents, it was necessary to prepare saturated solutions. Ninety-five per cent ethyl alcohol was chosen as the solvent because it provides a homogeneous phase with the dye and the test solutions. Other solvents which would provide mutual solubility such as absolute ethyl alcohol and ethylene glycol were considered, but when the solubility of the dyes in these solvents was studied (1) it was observed that no particular advantage would be gained by their use.

Test solutions were prepared, such that each milliliter of solution contained 3 mg. of metallic group. Twenty per cent chloride-free nitric acid, hydrochloric acid, and aqua regia were employed as solvents. The substances dissolved in 20 per cent nitric acid were Th(NO₃)₄, K₂Cr₂O₇, Hg(NO₃)₂.2H₂O, UO₂(NO₃)₂.6H₂O, Mg(NO₃)₂.6H₂O, Cu(NO₃)₂.3H₂O, Co(NO₃)₂.6H₂O, Mn(NO₃)₂, Pb(NO₃)₂, Bi(NO₃)₃.5H₂O, Al(NO₃)₃.9H₂O, Fe(NO₃)₃.9H₂O, Cr(NO₃)₃.9H₂O, Ni(NO₃)₂.6H₂O, AgNO₃, Zn(NO₃)₂.6H₂O, Zr(NO₃)₄.5H₂O, Y(NO₃)₃.6H₂O, Rh(NO₃)₃, Pd(NO₃)₂, Ce(NO₃)₃.6H₂O, Ti(NO₃)₃, Cs(NO₃)₂, Cd(NO₃)₂.4H₂O, and V₂O₅; those in 20 per cent aqua regia were OsO₄, IrCl₃, and Ru(NO)Cl₃; and those in 20 per cent hydrochloric acid were As₂O₃, Sb₂O₃, and MoO₃.

TABLE I. REACTION OF DYES WITH SOLVENTS

No.	20% Nitric Acid		20% Hydrochloric Acid		20% Aqua Regia	
	Spot paper	Spot plate	Spot paper	Spot plate	Spot paper	Spot plate
I	No change	RO spot	No change	RO spot	Dye bleached	Dye bleached
II	Pink stain	RO spot	RO stain	OR spot	Dye bleached	RO spot
III	ROT2 ring	ORT1 spot	ROT2	ORT1 spot	Dye bleached	RT2 spot
IV	Dye bleached	No change	Dye bleached	No change	Dye bleached	Dye bleached
V	Dye bleached	OYT1 spot	Dye bleached	OYT1 spot	Dye bleached	Dye bleached
VI	Dye bleached	No change	Dye bleached	No change	Dye bleached	Dye bleached
VII	Dye bleached ^a	No change	YOT2 spot	No change	Dye bleached	Dye bleached
VIII	Dye bleached	YOT2 spot	Dye bleached	YOT2 spot	Dye bleached	Dye bleached
IX	No change	YT2 spot	No change	YT2 spot	Dye bleached	Dye bleached
X	OT2 spot	RO spot	OT2 spot	RO spot	Dye bleached (pink ring)	Dye bleached
XI	Dye bleached ^a	OYS1 spot	Dye bleached ^a	OYS1 spot	Dye bleached	Dye bleached
XII	Dye bleached	OY spot ^b	Pink spot	OY spot ^b	Dye bleached	Dye bleached
XIII	Dye bleached	OT2 spot	Dye bleached	OT2 spot	Dye bleached	Dye bleached
XIV	VRT2 ring	RT2 spot	VRT2 ring	RT2 spot	Violet ring	Dye bleached
XV	Cinnamon spot	YO spot	Cinnamon spot	YO spot	OT1 spot	YO spot
XVI	Orange ring	OYS1 spot	Orange ring	OYS1 spot	Bright O ring ^c	Orange spot
XVII	No change	No change	No change
XVIII	No change	No change	No change

^a Slightly. ^b Faint. ^c Then greenish fugitive ring, changing to yellow spot.

O = orange; R = red; Y = yellow; V = violet; T = tint; S = shade (3).

In solution, molybdenum trioxide was transformed into the anion MoOCl_5^{--} (2) by dissolving the substance in 20 per cent hydrochloric acid, boiling the solution, and evaporating almost to dryness. Then 10 ml. of 20 per cent hydrochloric acid were added, and the solution was concentrated to about half the volume, cooled, and diluted in a volumetric flask to 50 ml. with 20 per cent hydrochloric acid.

Procedure

In analysis by the spot paper test, one drop of the alcoholic solution of the test reagent is placed on a piece of good quality filter paper and allowed to stand a moment. Then a drop of the test solution is placed on the center of the reagent spot. [In studying the effect of interfering anions, a drop or fraction thereof of the test solution of such an ion (chloride or tartrate) is placed on the reagent spot or drop before or after a drop of the test solution as desired. A solvent blank is used as a control.]

In analysis by spot plate tests, two drops of the test reagent are placed in a well of a porcelain spot plate. To this a drop of test solution is added.

Dilution tests are made by measuring a quantity of standard test solution and diluting by the proper solvent to a definite volume.

In the analysis of an unknown (2), the sample for analysis is dissolved in concentrated nitric acid and the solution evaporated to dryness. The residue is taken up in about 20 per cent nitric acid for use in spot paper or spot plate tests.

Data

The following dyes were studied in this investigation and are referred to by number in the discussion below:

- I. 5-(2-hydroxyphenylazo)-8-hydroxyquinoline
- II. 5-(3-hydroxyphenylazo)-8-hydroxyquinoline
- III. 5-(2-nitrophenylazo)-8-hydroxyquinoline
- IV. 5-(3-nitrophenylazo)-8-hydroxyquinoline
- V. 5-(4-nitrophenylazo)-8-hydroxyquinoline
- VI. 5-(2-chlorophenylazo)-8-hydroxyquinoline
- VII. 5-(3-chlorophenylazo)-8-hydroxyquinoline
- VIII. 5-(4-chlorophenylazo)-8-hydroxyquinoline
- IX. 5-(2,5-dichlorophenylazo)-8-hydroxyquinoline
- X. 5-(3-tolylazo)-8-hydroxyquinoline
- XI. 5-(2,6-dimethylphenylazo)-8-hydroxyquinoline

- XII. 5-(4-aronophenylazo)-8-hydroxyquinoline
- XIII. 5-(3-sulfophenylazo)-8-hydroxyquinoline
- XIV. 5-(1-sulfo-2-naphthylazo)-8-hydroxyquinoline
- XV. 5-(8-hydroxy-3,6-disulfo-1-naphthylazo)-8-hydroxyquinoline
- XVI. 5-(benzidinemonoazo)-8-hydroxyquinoline
- XVII. 5,5'-(benzidinedisazo)-8-hydroxyquinoline
- XVIII. 5-(3,3'-dimethoxybenzidinemonoazo)-8-hydroxyquinoline

The nitrates of aluminum, bismuth, cadmium, cerium, cesium, chromium, lead, magnesium, manganese, rhodium, silver, thallium, thorium, yttrium, zinc, and zirconium, and the chlorides of antimony and arsenic give negative tests with all the dyes. Ruthenium nitrosochloride and uranyl nitrate give negative tests also. Molybdenum does not give tests which are of analytical significance. Copper gives mediocre tests with dyes II and X.

Nickel gives mediocre spot paper tests with IV, VII, VIII, and X. Mercury and palladium give tests with VIII, which may interfere with the test with nickel. Osmium gives no tests, and iridium gives a useless test with II. On spot paper cobalt gives very doubtful tests with II, X, and XIII. Iron gives identical results with all the dyes on spot paper, but the color change is so fugitive that the tests are of no value. In both spot paper and spot plate tests, dichromate ion gives excellent results with all the dyes except XVII and XVIII. In certain spot plate tests, the addition of hydrochloric acid after the test drop enhances the significance of the results.

Specific Tests

MERCURY. With II, mercury gives a "violet-red" spot paper stain which is destroyed if treated with hydrochloric acid. On a spot plate, a "red-violet shade two" precipitate (3), which is soluble in hydrochloric acid, forms immediately. This test is similar to that for palladium except that the precipitate or stain formed with palladium is insoluble in hydrochloric acid.

A "red-violet tint two" spot of excellent intensity develops slowly on spot paper with VII. An "orange-red tint one" color develops immediately on a spot plate, and a "violet-red tint

TABLE II. REACTIONS OF METALS WITH DYES

Dye No.	Metals										Test
	Hg ⁺⁺	Cu ⁺⁺	Pd ⁺⁺	Ni ⁺⁺	MoOCl ₅ ⁻⁻	VO ₂ ⁺ or VO ₃ ⁻	Co ⁺⁺	Fe ⁺⁺⁺	Cr ₂ O ₇ ⁻⁻		
I	GY, r: E	RO, r: C	GY, r: A	Neg.	O, r: D	GO, s, r: D	Neg.	Gr, r, f: D	RO, r: A	Paper Plate	
	ORS2, s: D	ROS2, s: B	VRT1, s: A	Neg.	YOS2, s, f: D	YOS2, s, f: D	YGrS2, s, f: E	VRT2, s: A		
II	VR, s: A	RVS1, r: B	RVS2, r: A	RT1, r, f: C	YOS1, r: C	OYS1, r: B	O, r: C	GYs2, r, f: D	VR, s: A	Paper Plate	
	RVS2, s: A	RT1, s: C	RVS2, p: A	Neg.	VBS1, s: C ⁺	BrGr, p: A	Neg.	GY, s, f: D ⁺	VR, s: A ⁺		
III	Neg.	Neg.	Neg.	Neg.	Neg.	GY, r, f: D	Neg.	GYs1, r, f: C	Neg.	Paper Plate	
	RT1A, s: C	Neg.	Neg.	GY, s, f: D		
IV	OY, r, f: D	Neg.	ORT1, r: C	YOT1, r: B	Neg.	YT1, r: D	Y, r, f: D	GY, r: B	VRS2, r: B	Paper Plate	
	OT1, s: D	Neg.	RT1, s: B	Neg.	Neg.	Neg.	Y, s, f: D ⁺	GY, s, f: D ⁺	VRT1, s: Aa		
V	Neg.	Neg.	OT2, s: C	Neg.	Neg.	Neg.	Neg.	Neg.	V, s: B	Paper Plate	
	ROT2, s: D	Neg.	RT2, s: B	Neg.	VRT1, s: Aa		
VI	Neg.	Neg.	VS2, r: B	Neg.	Neg.	GY, r: D	Neg.	GYs1, r, f: D	VRS2, r: D	Paper Plate	
	O, s: C	Neg.	V, s: A	Neg.	YG, s, f: C ⁺	GY, s, f: D ⁺	RT1, s: Aa		
VII	RVT2, s: A	OT2, s, r: C	VRS1, s: C	ORT2, r: B	Neg.	GYs1, r, f: D	Neg.	GYs1, r, f: D	VRT2, r: A	Paper Plate	
	VRT2, p: B	RO, s: E	RT1, p: A	Neg.	VRT2, r: B	YOS1, s, f: C ⁺	YOS1, s, f: E ⁺	RT1, s: A ⁺		
VIII	ORT2, s: B	Neg.	ORT2, r: C	ORT2, r: B	Neg.	YGT2, r, f: D	Neg.	GYs2, r, f: C	ORT2, r: A	Paper Plate	
	ORT1, s: A	Neg.	RT1, s: B	Neg.	Neg.	Neg.	YS2, s, f: B ⁺	R, s: Aa		
IX	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	GYs1, r, f: D	Neg.	Paper Plate	
	OT2, s: D	Neg.	Neg.		
X	VR, s: A	VRT1, s: B	BR, s: C	RS1, r: B	VRT1, s: D	GYs1, r, f: D	OY, r: B	GYs1, r, f: D	VRT1, s: A	Paper Plate	
	RS2, s, p: A	Neg.	RS2, p: A	Neg.	B', r: C	YG, s, f: D ⁺	Neg.	GY, s, f: D ⁺	OR, s: A		
XI	OY, r, f: D	O, r, f: D	RT2, s: B	YO, r, f: D	Neg.	GYT1, r: C	Neg.	GY, r: C	RT2, r: C	Paper Plate	
	YO, s: D	Neg.	V, p: B ⁺	Neg.	Neg.	GY, s, f: D ⁺	RT1, s: A ^a		
XII	OT1, r: B	ROT1, r: D	VRT1, s: A	ROT2, r, f: E	ORT2, r, f: E	OT2, r, f: D	OT1, r: D	VT2, r: C	VRT2, s: A	Paper Plate	
	OR, p: A	Neg.	OR, s: A ⁺	Neg.	Neg.	VS1, s, f: E	Neg.	GY, s, f: D ⁺	VRT1, s: A ^a		
XIII	ORT2, r, f: B	RVT2, r: D	VRT2, r: D	ORT2, r, f: D	Neg.	Neg.	O, r, f: D	Gr, r, f: E	RT2, s: C	Paper Plate	
	ORT2, s: B	OT2, s: E	OT1, s: B	Neg.	Neg.	Neg.	GT2, s, f: E ⁺	RVT2, s: B ⁺		
XIV	Neg.	Neg.	VT1, r: C	RVT1, r: E	Neg.	Neg.	Neg.	BT2, r, f: E	Neg.	Paper Plate	
	VRT1, s: C	VRT1, s: D	RVBT, s: C	Neg.	Neg.	B', s, f: C ⁺		
XV	RVT1, s: A	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	VT2, s: A	Paper Plate	
	VR, s, p: B	Neg.	Neg.	Neg.	Neg.	Neg.	VR, s: C ^a		
XVI	B'T2, s: A	VBT2, r, f: E	RVT2, s: C	VT2, r, f: D	Neg.	YGT1, s: A	RVT2, s, f: D	Neg.	G, s, r: B	Paper Plate	
	RVT1, s, p: B	Neg.	YOS1, p: A	Neg.	YS1, s: A	Neg.	OG, s: B		
XVII	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Paper Plate	
XVIII	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Paper Plate	

R = red; O = orange; Y = yellow; G = green; B' = blue; V = violet; Br = brown; Gr = gray; S = shade; T = tint (3).
 r = ring; s = spot; f = fugitive; p = precipitate; + = tartrate obscures; a = hydrochloric acid enhances.
 Grade rating of tests: A = excellent; B = good; C = fair; D = poor; E = very poor.

TABLE III. LIMIT OF DETECTION

(Milligrams per milliliter of solution)

Dye No.	Mercury		Palladium		MoOCl ₅ ⁻		Copper		Vanadium		Cr ₂ O ₇ ⁻	
	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop	Spot	Drop
I	3	1	0.1	0.1	+	+	0.3	+	0.3	3	0.3	0.1
II	0.3	0.1	0.1	0.1	3	3	0.3	+	0.3	0.3	0.3	0.1
III	0.3	3	+	+	..	+	..	+	0.3	+	+	1 ^a
IV	1	0.5	0.3	0.3	..	+	..	+	3	+	0.3 ^a	0.3 ^a
V	1	0.5	0.1	0.1	..	+	..	+	3	+	0.3 ^a	0.3
VI	+	3	0.1	0.3	..	+	..	+	0.3	+	0.3 ^a	0.3 ^a
VII	0.3	0.5	0.1	0.1	..	+	+	1	0.3	3 ^b	0.3	0.3 ^a
VIII	1	0.5	0.1	0.1	..	+	..	+	+	0.3	0.3-0.1 ^a	0.3 ^a
IX	+	+	+	0.3	..	+	..	+	+	..	+	0.3
X	0.5	0.5	0.1	0.1	3	+	0.3	+	0.3	3	0.3-0.1 ^a	0.3-0.1
XI	+	3	0.3	0.3	..	+	..	+	0.3	..	0.3	0.3-0.1
XII	0.5-1	3	0.1	0.3-0.1	3	3	0.3	0.3	0.3	..	0.3 ^a	0.3 ^a
XIII	3	3	0.3-0.1	0.3	..	+	..	+	+	..	+	0.3 ^a
XIV	3	3	0.3	0.1	1	+	0.3	0.3	0.3	..	+	0.1
XV	0.5-1	0.3	+	3-1	..	+	..	+	+	3	0.3	0.3
XVI	0.3	0.1	0.3	0.3-0.1	..	+	0.3	1	0.3	0.3-0.1	0.3	0.3

^a HCl added after test drop. ^b Fugitive. + = Negative test obtained with 3 mg. per ml. concentration.

two" precipitate forms, both of which are destroyed by hydrochloric acid. This latter fact serves to distinguish mercury from palladium.

On a spot paper, an "orange-red tint two" spot with a fugitive ring of the same color forms with VIII. An "orange-red tint one" spot, the color of which is destroyed by hydrochloric acid, forms immediately on a spot plate. This is a good test, but the spot plate test is probably the better. Palladium gives a test with the dye too, but the two metals may be distinguished readily.

A "violet-red" spot forms on spot paper immediately with X. On a spot plate a "red shade two" spot forms, and a precipitate settles out. If hydrochloric acid is added to the spot paper or spot plate test, the color or the precipitate is destroyed. This fact serves to distinguish mercury from palladium.

On spot paper, XII forms an "orange tint one" ring which is destroyed by hydrochloric acid. An "orange-red" precipitate which is soluble in hydrochloric acid forms when a spot plate test stands about a minute. This test is characteristic for mercury; probably the spot plate test is the better. Copper may interfere with the test.

A "red-violet tint one" spot forms immediately on spot paper with XV. On a spot plate, a "violet-red" spot forms immediately, and a precipitate of the same color settles out. In both tests hydrochloric acid destroys the color and the precipitate.

PALLADIUM. A marked "olive-green" spot which changes to an "olive-green" ring around a pink spot forms on spot paper with I. On standing, the ring turns to a purple color. On a spot plate, a brownish gray precipitate settles out immediately from a "violet-red tint one" spot. Hydrochloric acid causes a part of the precipitate to dissolve, and the mother liquor to assume an orange color.

Palladium gives the same reaction as mercury with II, both on spot paper and on a spot plate. The only way to distinguish palladium from mercury is by the behavior of the spot on paper or spot plate tests towards hydrochloric acid. With palladium, hydrochloric acid has no effect, but with mercury the test is destroyed.

On a spot plate, an "orange shade one" spot forms with VI, and a brown precipitate deposits immediately, which, on standing, assumes a violet or purple color. The precipitate is somewhat soluble in hydrochloric acid.

On a spot plate, a "red tint one" spot, from which a purple precipitate settles, forms immediately with VII. Hydrochloric acid destroys the color of the spot and causes the color of the precipitate to change to brown. Tartrate ion has no effect on the test.

On spot paper, a "violet-red" spot develops rapidly with X. On a spot plate, a "red shade two" spot forms immediately, and a precipitate of the same color separates. This test resembles that for mercury, but palladium can be distinguished from mercury by the fact that the color reactions, in the case of palladium, are unaffected by treatment with hydrochloric acid.

A "yellow-orange shade one" spot forms immediately on a spot plate with XVI. On standing, a brown precipitate deposits. Tartrate ion masks the test somewhat by retarding the formation of a color and a precipitate.

VANADIUM PENTOXIDE, VANADYL ION (VO₂⁺), AND METAVANADATE ION (VO₄⁻). With II, a distinctive "orange-yellow shade one" ring forms on spot paper around a faded stain. If hydrochloric acid is added to the test, a "red-orange" ring forms around a pale "red-violet" stain. On standing, the stain itself becomes grayish and the ring begins to fade into the spot. On

a spot plate, a distinctive brownish gray precipitate deposits almost immediately. Tartrate ion has no effect on the test; chloride ion has only a very slight effect.

On spot paper, a very brilliant and characteristic "yellow-green tint one" spot forms with XVI. On a spot plate, a distinctive, rather intensive "yellow shade one" spot forms immediately. In either test, the presence of halogen has no effect.

Summary

In practically all cases, the presence of chloride ion in the test solution obscures the results. In certain cases, particularly with dichromate, cobalt, and nickel, hydrochloric acid enhances the results when added to the dye spot after the test solution. There are a few cases, particularly with palladium

and mercury, where the behavior of the test on treatment with hydrochloric acid serves as the only means of distinguishing between the metals. Tartrate ion, contrary to the literature, seems in most cases to have no effect on the test.

It has been claimed that these azo derivatives of 8-hydroxyquinoline give, except in a few minor cases, consistent reactions which are specific for mercury, copper, palladium, nickel, and molybdenum as MoOCl₅⁻ ion. The results of this research do not bear out this statement. On both spot plate and spot paper tests, mercury and palladium give color reactions with practically all the dyes studied, but only a few tests are sufficiently characteristic and intense to be considered specific. On a spot paper test, copper and nickel show a few color reactions of doubtful value, while on a spot plate no tests are observed. In either test, molybdenum gives only a few color reactions of no possible value in analytical work.

In view of this present research, it seems that the statement that polar groupings para to the point of coupling in the aromatic nucleus cause a more positive reaction should be modified so as to include only those groupings, such as hydroxyl, amino, sulfo, and carboxyl, which tend to increase the solubility of a compound in a semipolar or polar solvent such as alcohol or water. The results of this investigation are not entirely in accord with the fifth conclusion of Gutzeit and Monnier as stated above.

Condensed structures, when attached to 8-hydroxyquinoline through an azo linkage as with XIV, XV, XVI, XVII, and XVIII, tend to decrease the usefulness of the dye as an analytical reagent even though such naphthyl and biphenyl structures do contain substituents such as hydroxyl, sulfo, or amino groups which tend to increase solubility. The last two dyes mentioned are so insoluble in alcohol that there is not a sufficient concentration of active grouping (8-hydroxyquinoline) to give a positive test even with metals most likely to react.

Some new tests have been developed which may serve in the identification of metals. One reagent (XVI) has been developed for vanadium; six (II, VII, VIII, X, XII, and XV), for mercury; and six (I, II, VI, VII, X, and XVI), for palladium.

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RECEIVED July 11, 1938. Presented before the Microchemical Section at the 96th Meeting of the American Chemical Society, Milwaukee, Wis., September 5 to 9, 1938.

Determination of Carbon and Hydrogen

On Micro- or Semimicrosamples with One Compact and Movable Apparatus

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RECENTLY (1) the authors described a movable and easily constructed apparatus for the determination of carbon and hydrogen, designed to analyze a 70-mg. sample. This apparatus has now been successfully scaled down for application to microsamples.

The apparatus in its present form (Figures 1 and 2) takes up a maximum of 57.5 cm. (23 inches) of desk space when the absorption tubes are not attached. It can be used for samples of from 2.5 to 35 mg. without increasing the combustion time appreciably beyond that for the standard combustion of microsamples. With larger samples, the combustion time is increased beyond a reasonable amount. When a microbalance is available microsamples (3 to 6 mg.) are weighed for analysis; otherwise, a 20- to 30-mg. sample is weighed using an analytical balance (weighing to 0.1 mg.) or a semimicrobalance (weighing to 0.01 mg.) for greater accuracy. The time of combustion for a microsample is usually 40 minutes; for a semimicrosample, 55 minutes. A copper oxide spiral is not necessary behind the boat for samples of either size.

Although the outfit was designed for microanalysis, with some minor alterations it could be used for samples ranging up to 35 mg., permitting the use of an ordinary analytical balance without losing efficiency as a microcombustion outfit. The apparatus is now mounted on a metal frame cast from aluminum with an iron base.

Apparatus

Figure 2 illustrates the present setup of the apparatus, its dimensions, and the filling of the tube. The following improvements may be noted:

1. The capacity of the bulb in the gasometer has been increased to 2 liters. A gasometer of this size can deliver about 650 cc. of oxygen when the gage reads 25 cm. of mercury. Less frequent fillings of the gasometer are necessary, and the bubble rate remains constant throughout the combustion.

2. Lead chromate has been eliminated from the preheater. Its presence is unnecessary and is objectionable in that it shortens the life of the Pyrex tube. The heating coil is now in parallel with the main heating coil, making temperature control easier. The preheater coil is prepared by winding nine turns of No. 28

wire to the inch for a space of 12.5 cm. (5 inches) to give a temperature of 550° C.

3. The bubble counter has been redesigned and placed behind the scrubber. This makes hydrogen results more constant.

4. Indicating Drierite, instead of calcium chloride, has been found to have advantages in the scrubber. The internal diameter of the scrubber has been reduced to 9 mm.

5. A combustion tube 9 mm. in internal diameter and of hard combustion tubing is convenient for analyzing any sample of from 2.5 to 35 mg. If the apparatus is to be used exclusively, for microanalysis, standard tubing 6 to 7 mm. in internal diameter may be substituted. In numerous tests, the use of the narrower tubing has shown no apparent advantage.

6. The method of obtaining a differential in temperature between the end and main part of the heating unit has been changed. Previously, the turns were wound at greater intervals at the cooler end. This same result may be attained more readily by changing the gage of the wire at the cooler end and winding as for the main part of the tube. The total length of the heating coil is 32.5 cm. (13 inches). For the first 23.75 cm. (9.5 inches) No. 26 (B. & S. gage) Nichrome wire is wound. The turns are spaced at 0.6-cm. (0.25-inch) intervals except for the very beginning where, in order to compensate for end cooling, four turns are taken in the first 1.25 cm. (0.5 inch). The end is then spliced to No. 20 wire and the winding is continued for the last 8.75 cm. (3.5 inches). To allow for conduction from the hotter part of the coil, it was found necessary to take only one turn of the No. 20 wire for the first 1.25 cm. (1 inch). The turns for the remaining 6.25 cm. (2.5 inches) are taken at 0.6-cm. (0.25-inch) intervals except for the very end. To allow for the end cooling effect, three turns were taken for the last 0.94 cm. (0.375 inch).

A simple calculation will indicate why these diameters were chosen. With constant current, the heat developed in a wire is proportional to its resistance and the resistance is inversely proportional to the square of the radii of the wires employed, if the winding is evenly spaced around the same tube. No. 26 wire at 0.6-cm. (0.25-inch) intervals was found to be suitable for the first 25 cm. (10 inches) (675° to 700° C.). For the next 7.5 cm. (3 inches) a temperature of about 200° C. had to be maintained. Since the same materials (constant specific heat and rate of radiation) were used throughout the combustion coil, it was safe to assume that the heat developed was proportional to the temperature and hence the following proportion was set up:

$$\frac{(\text{Radius of No. 26 wire})^2}{(\text{Radius of desired wire})^2} = \frac{(0.00797 \text{ inch})^2}{(X \text{ inch})^2} = \frac{200^\circ \text{ C.}}{675^\circ \text{ C.}}$$

On solving for the unknown one obtains 0.041 cm. (0.0164 inch), which is closest to the radius of No. 20 wire. That the

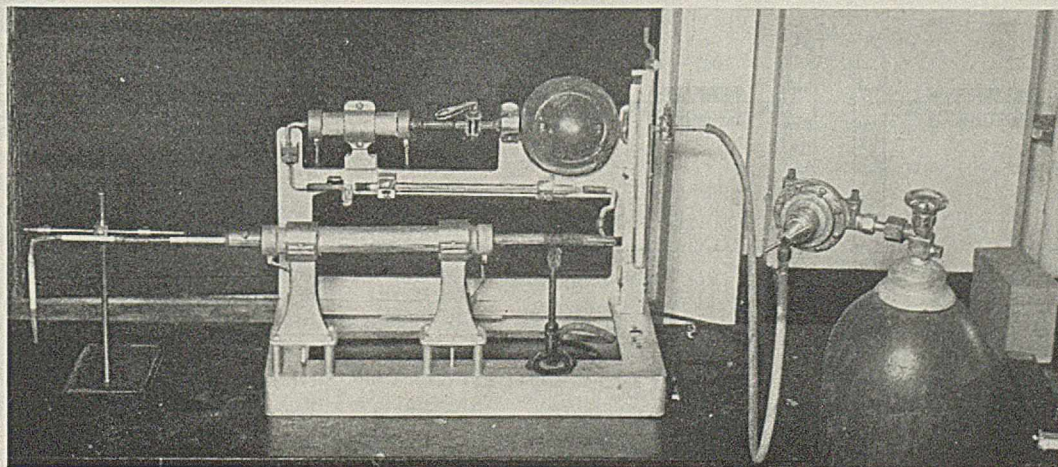


FIGURE 1. APPARATUS SETUP FOR MICROANALYSIS

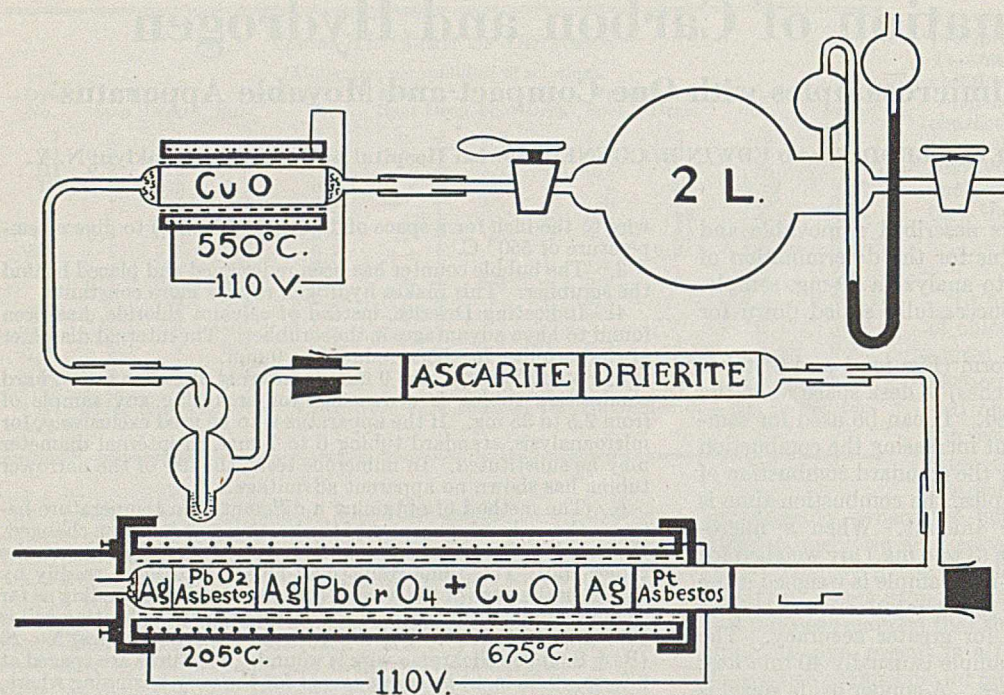


FIGURE 2. SCHEMATIC DIAGRAM OF COMBUSTION APPARATUS

reasoning is correct was evidenced by the fact that No. 20 wire for the last 6.25 cm. (2.5 inches) gave the required temperature ($200^{\circ}\text{C}.$) within 10° when spaced at the same interval 0.6 cm. (0.25 inch) as the No. 26 wire. A smoothly uniform temperature is thus readily obtainable in both parts of the tube. To improve its appearance, the insulation around the heating coils is now cast in a split metal mold.

7. In order to avoid the condensation of moisture at the mouth of the combustion tube, a split metal tube hinged on one side is attached to the heating coil. When attaching the absorption tubes, the upper part of this metal tube is moved back on its hinges and replaced after connection has been made. This split tube, kept warm by conduction from the heating coil, is long enough to force the water directly into the absorption tube. An auxiliary metal tube, cut from a cork borer of the proper dimensions, may be used by sliding part of it in and out of the split tube if any additional length is needed.

The connection between the combustion and absorption tubes is made by means of the usual heavy red nitrometer tubing, previously heated to $110^{\circ}\text{C}.$ and carefully cleaned inside and out. After more than 6 months' continuous use, no apparent deterioration had taken place. During the combustion, this

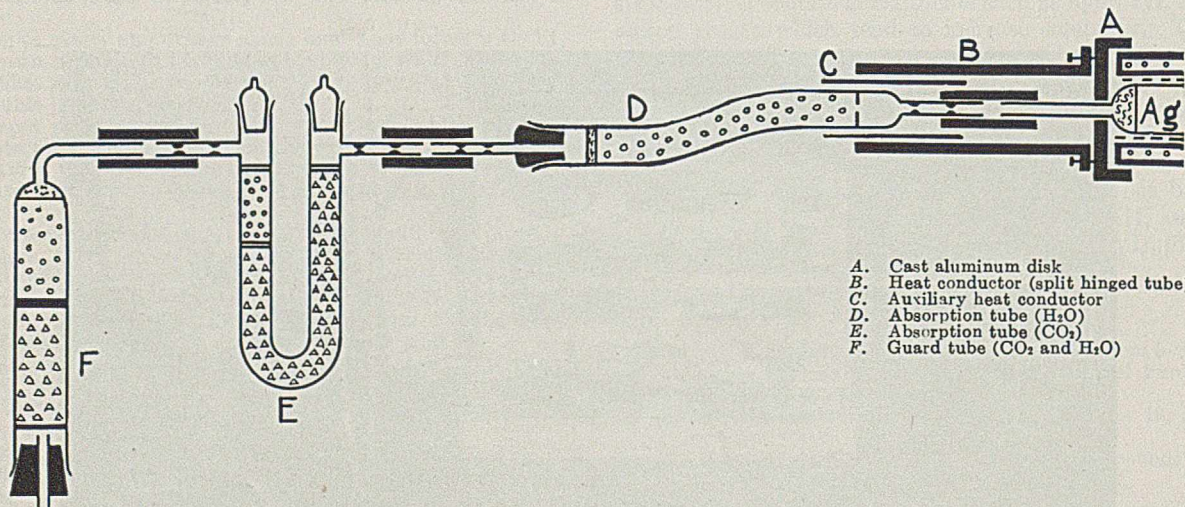
with dilute sulfuric acid to remove traces of zinc, filtered, washed, and dried in an oven. The finely divided silver is then heated at $675^{\circ}\text{C}.$ (in the combustion train) for 1 hour, in order to avoid any shrinkage which may occur in the tube later. It is then allowed to cool and transferred to a bottle for further use.

9. For analysis of semimicrosamples, absorption tubes patterned after the usual microabsorption tubes were used (Figure 3). For microdeterminations, tubes of standard size were used.

10. The design of the support for both micro- and semimicro-absorption tubes on one small ring stand is worthy of note (Figure 1).

Procedure and Results

For the combustion of the microsamples the standard procedure is used, 10 minutes for the first combustion and 10 minutes for reheating in order to assure complete combustion. The washing time is approximately 20 minutes, making the complete combustion time about 40 minutes. On samples of about 25 mg. the two combustion times combined



- A. Cast aluminum disk
- B. Heat conductor (split hinged tube)
- C. Auxiliary heat conductor
- D. Absorption tube (H_2O)
- E. Absorption tube (CO_2)
- F. Guard tube (CO_2 and H_2O)

FIGURE 3. ABSORPTION TUBES FOR SEMIMICROSAMPLES
Designed for weighing on balance pans

tubing is subjected to temperatures just below the boiling point of water.

8. The combustion tube is now filled as shown in Figure 2. All the asbestos plugs need not be wider than 1 to 2 mm. Precipitated silver may be used rather than the usual silver wire. It was observed that compounds with a high percentage of chlorine (more than 40 per cent) consistently gave slightly high results for carbon when silver wool, wire, or foil was used. The silver filling as used in this tube absorbed 300 mg. of chlorine (calculated from the weights and percentage of chlorine of the compounds used) before any indication of breakdown was observable. The silver could then be regenerated in the usual way. For the usual run of analyses silver wire may serve as well.

The precipitated silver may be prepared by treating silver nitrate with zinc dust (less than theoretical) and heating on a water bath. The precipitated silver is filtered off, boiled

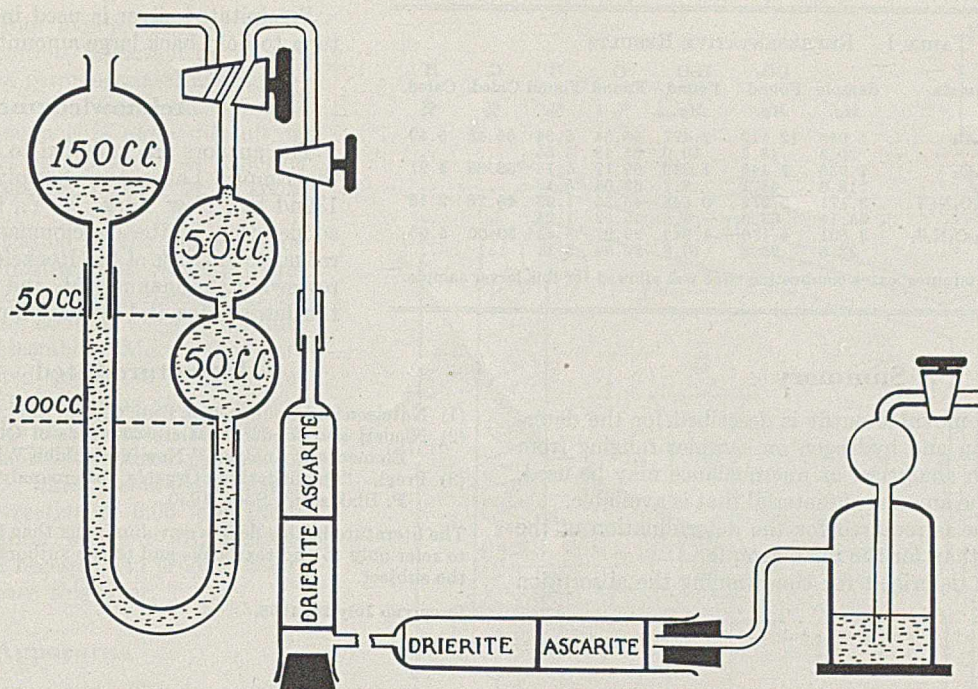


FIGURE 4. DESIGN OF ASPIRATOR FOR CONDITIONING ABSORPTION TUBES

are about 30 minutes and the washing time is about 25 minutes, making a complete combustion time of about 55 minutes.

In the combustion of the microsample 175 cc. of oxygen are used, and 325 cc. of oxygen are used for the combustion of the semimicrosample. In the case of the semimicrosample the oxygen has to be passed at the relatively rapid rate of about 5.5 cc. per minute. This can easily be achieved because the resistance of the semimicrotubes is much less than that of the microtubes. In the authors' apparatus the bubble rate was maintained at about 40 bubbles per minute. When the microtubes were attached the rate was maintained at about 4 cc. per minute or a little less than 2 bubbles per second.

The bubble rate is set at the start of the combustion. The position of the adjusting stopcock is not changed until the combustion is finished, even though at times it may vary temporarily when burned gases gather in the tube. Where combustion is difficult—i. e., with samples of high chlorine or sulfur content—the bubble rate must be slower and the time of combustion longer.

For best results (2) it is good practice, before and after the combustion, to aspirate air (dried and free of carbon dioxide) through the absorption tubes, in order to weigh the tubes filled with air rather than oxygen. For this purpose many experimenters have used the Mariotte bottle. The authors have designed an apparatus which avoids some of the disadvantages of the Mariotte bottle—the need to be present when the required amount of water has gone into the graduated cylinder, the inconvenience encountered in the refilling of the bottle, and the change in bubble rate and hence in time for the required 50 cc. as the level is lowered in the bottle. The apparatus recommended is automatic, drawing through the required amount and stopping of its own accord. There is no pouring of water and the time to deliver the required volume is always the same. A glance at Figure 4 will indicate the design.

When the reservoir, *A*, is lowered to the required level, the amount of air desired will be drawn through and movement will cease. The two-way stopcock may then be turned so that when

the reservoir is raised, the aspirated air is expelled. The stopcock is then returned to its original position and the apparatus is ready for use again. Instead of the 50-cc. bulbs, a 100-cc. graduated cylinder tube may be used. The bubble rate is regulated by means of a glass stopper, pinchclamp, or capillary located behind the aspirator. One filling of the tube as shown or the graduated cylinder will aspirate two sets of microtubes or one set of semimicrotubes. For microdeterminations, 50 cc. of air are passed through in 10 minutes. The tubes may then be placed directly on the balance and weighed without further delay. For the semimicrotubes 100 cc. of air are passed through in the same time (10 minutes) and the tubes are weighed directly. Both semimicro- and microtubes should be wiped carefully before weighing.

With two sets of tubes about six determinations of either micro- or semimicrosamples may be readily performed in one day. Table I shows representative results obtained on the same outfit by alternating from micro- to semimicrosamples of compounds with a variety of characteristics. A Kuhlman microbalance was used for the microsamples. The semimicrosamples were weighed to 0.1 mg. by means of an analytical balance fitted with a magnetic damper. It is apparent that for the semimicrosamples the accuracy of the results is limited by the accuracy of the weighing.

Discussion

It is apparent that with minor differences the procedure and time are almost the same for micro- and larger samples using this apparatus. In the authors' experience both sizes of sample have given consistent results. The choice therefore depends upon the amount of material available and whether one is to use the micro- or semimicrobalance. For instructional purposes this apparatus has the advantage that one may learn the technic of analysis on semimicrosamples with the aid of an ordinary balance and then transfer the same procedure to the determination of microsamples; the only new procedure to be learned is the operation of a microbalance.

The apparatus retains the advantages of being compact and movable. It may be stored without dismantling and may be set in operation on little notice.

TABLE I. REPRESENTATIVE RESULTS

Substance	Formula	CO ₂		H ₂ O		C		H	
		Sample Mg.	Found Mg.	Found Mg.	Found Mg.	Found %	Found %	Calcd. %	Calcd. %
Resorcinol	C ₆ H ₄ O ₂	5.040	12.112	2.497	65.54	5.54	65.43	5.49	
Benzoic acid	C ₇ H ₆ O ₂	20.2	48.5	10.0	65.48	5.55	65.43	5.55	
		2.938	7.446	1.249	69.12	4.76	68.85	4.91	
<i>p</i> -Nitrobenzoyl chloride	C ₇ H ₄ O ₂ NCl	19.0	48.1	8.7	69.04	5.12	68.85	5.12	
		3.171	5.272	0.548	45.35	1.93	45.28	2.16	
Cystine	C ₆ H ₁₂ O ₄ N ₂ S ₂	38.1 ^a	63.6	6.6	45.52	1.94	45.52	1.94	
		3.801	4.176	1.845	29.97	5.43	30.00	5.00	
		23.5	25.8	10.8	29.94	5.14	

^a As a safeguard 15 minutes' extra combustion time was allowed for this larger sample.

Summary

A compact and movable outfit is described for the determination of carbon and hydrogen on samples ranging from 2.5 to 35 mg. An analytical or microbalance may be used, depending upon the amount of material that is available.

Little more time is required for the determination of the semimicrosample than for the microsample.

An aspirator is described for conditioning the absorption tubes.

Precipitated silver is used in the combustion tube to hold back large amounts of halogen.

Acknowledgment

The authors are indebted to Mr. Weiskopf of the Empire Laboratory Supply Co., 559 West 132nd St., New York, N. Y., for his continued coöperation in the development of this apparatus, to A. Elek of the Rockefeller Institute for reviewing the manuscript, and to B. Kramer of the Jewish Hospital for his support.

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The literature in this field is so voluminous that it has been decided to refer only to two textbooks and to the authors' previous paper on the subject.

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Determination of Iodine in Biological Materials

Refinements of the Chromium Trioxide Oxidation Method

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QUANTITATIVE studies of iodine metabolism require adequate analytical procedures, adapted to the determination of the minute amounts of iodine present in biological materials. Owing to the complexity of former methods (10), difficulties have been experienced in obtaining consistent results, while comparative studies from different laboratories have shown considerable variation (2).

Most procedures for destroying the organic matter, preparatory to actual extraction and determination of the iodine, have involved combustion in a closed system or basic ashing. A procedure developed by Leipter (8) in 1933, however, involved oxidizing the organic matter, and all the contained iodine to iodine pentoxide, by means of chromium trioxide in a sulfuric acid medium and in the presence of ceric sulfate as a catalyst. Leipter's method also employed steam distillation in partial vacuum to separate the small amounts of iodine from the sulfuric acid solution, after the iodine pentoxide and excess chromium trioxide had been reduced by arsenious oxide.

Trevorrow and Fashena (12) employed potassium dichromate instead of chromium trioxide as the oxidizing agent, since chromium trioxide usually contains iodine and is difficult to purify. They also found that the use of arsenious oxide resulted in unwarranted high iodine values, and consequently substituted phosphorous acid in its place as the reducing agent. Later (3), moreover, they found that their former method was not quantitative and replaced the vacuum-steam distillation by a combination of aeration and distillation.

The authors have devised a simple method for preparing

chromium trioxide of low iodine content. Ceric sulfate as a catalyst may be omitted in analyses of blood, urine, feces, thyroid gland, and milk of lower iodine content than approximately 1 mg.

The chromium trioxide method is not directly applicable to biological specimens which contain very minute concentrations of iodine. Thus, for the accurate analysis of mixed dried food, combustion in oxygen by the von Kolnitz and Remington modification (7) of the Karns procedure (5) precedes chromium trioxide oxidation (9). This makes convenient the oxidation of several hundred grams of material which is subsequently completed in the chromium trioxide procedure.

Iodine may be separated from the chromic sulfate and sulfuric acid solution by a simple distillation procedure. [C. D. Stevens of the DeCoursey Clinic of Cincinnati visited the authors' laboratory to investigate their procedures for the microdetermination of iodine. He later published a procedure employing the simple distillation (11).] The apparatus, designed for making this distillation (Figure 1), is easier to manipulate and more compact than either that of Leipter or of Fashena and Trevorrow.

Phosphorous acid is most effective as a reducing agent in the quantitative recovery by simple distillation of the smaller, more "biological" amounts of iodine. Larger amounts (2 mg. in 100 ml. of sulfuric acid) are only 90 to 95 per cent recovered when this reagent is employed (9). The use of oxalic acid (1) may result in the distillation of reducing substances.

A permanganate procedure, proposed by Groak (4) to

prepare iodate from iodide, involves oxidation in a basic solution, reduction by nitrous acid of the excess permanganate, and subsequent reduction of the excess nitrous acid with urea. Although it is more difficult to apply than either the bromine or chlorine procedures, it has been found to be more accurate (9).

Further investigation of the starch-iodine reaction (9) indicates that reagents, presumed to be iodine-free as determined by this principle, may contain varying amounts less than that detectable. Moreover, a part of this undetected iodine is actually recovered during determinations and thus may increase the results to the extent of 0.04 to 0.05 microgram of iodate iodine per ml. of titration solution. Since starch-iodine shows this property, correction of 0.06 microgram per ml. of titration solution (3), for the amount of iodine necessary to produce color, would only increase this error.

Apparatus

DISTILLATION APPARATUS. This is presented in Figure 1. (It may be obtained from the Leonard Glass Works, 1432 Minnesota Ave., Columbus, Ohio.) The digestion and distillation flask, I-a, may be of any size from 300 to 1200 ml. I-c is a standard joint of 30 mm. The coil condenser, I-g, has a dew-collecting cup, I-h, attached. Tubes having the following respective inside and outside diameters are recommended for the various pieces: I-b, 3 and 9 mm.; I-d, 3 and 6 mm.; I-f, 11 and 15 mm.; and II-d, 13 and 15 mm.

The apparatus may be mounted on one stand. It is washed by drawing water through the condenser into a flask with a stopper fitted for the joint.

II presents the entrainment trap, designed for this distillation. Its efficiency has been tested and has been found to compare well with that of other entrainment traps with larger or more intricate construction. Vapors on leaving the flask enter at II-a, follow the concentric tube around tube II-d, and enter tube II-d through opening II-c. The concentric tube is closed off at II-b, between II-a and II-c. Three small holes, 0.2 mm. in diameter, are located at II-e, the bottom of II-d, in order to permit condensed liquid to flow back into the flask. The concentric tube should have an inside cross-section area of approximately 30 sq. mm.

In III is shown a most useful type of antibump, which is easily made by first sealing a 3-mm. glass rod onto a glass tube of 3-mm. inside diameter and then cutting the tube 5 mm. from the closure and the rod at whatever length is suitable.

BURET. A buret of the Koch type (6), capable of measuring amounts up to 1 ml. and by which one may estimate 0.001 ml., is adequate. Titrations are conveniently made in front of white paper before a 125-watt light bulb.

Reagents

It is usually necessary to purify those reagents which are used in large amounts. Solutions should be used because of possible heterogeneity of solids with respect to significant minute amounts of iodine.

The reagents used in the analysis of 25 ml. of blood should contain less than 0.16 microgram of iodine. The nondetectable iodine (starch-iodine reaction) is determined by difference in titrating a known barely detectable amount of iodine, added at the titration. Reagents 6 to 12, inclusive, should contain a nondetectable amount of iodine when analyzed in quantities 5 to 10 times those used in the analysis of blood.

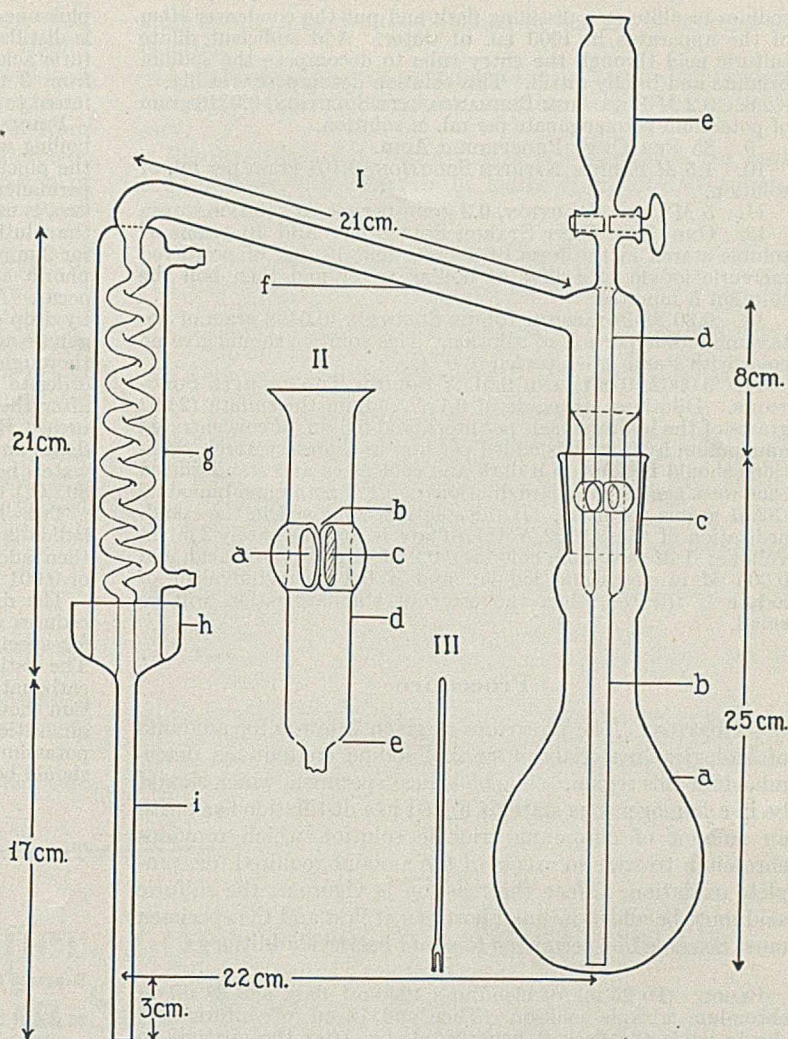


FIGURE 1. DISTILLATION APPARATUS

1. **DOUBLE-DISTILLED WATER.** Satisfactory water may be prepared by redistilling, in an all-glass apparatus, ordinary distilled water containing approximately 1 per cent of potassium hydroxide.

2. **CONCENTRATED SULFURIC ACID.** C. P. sulfuric acid usually contains only traces of iodine. By mixing 10 ml. of concentrated hydrochloric acid with 1 liter of technical sulfuric acid and boiling slowly for 30 minutes, one can prepare this grade of acid satisfactory for analysis.

3. **10 M CHROMIUM TRIOXIDE SOLUTION.** Place 1 mole of recrystallized potassium dichromate of low iodine content in the form of large crystals in a weighed 1-liter flask. Heat the potassium dichromate and 3.3 moles of sulfuric acid separately to 160° C. in an oven. Then pour the sulfuric acid into the potassium dichromate as nearly instantaneously as possible. The reaction quickly becomes violent and the chromium trioxide formed liquefies. Stir slowly until the mixture cools to 175° C. Then pour off the sulfuric acid solution and wash the solid chromium trioxide with 0.5 mole of 65 per cent sulfuric acid. The yield is from 80 to 90 per cent. Add 0.6 ml. of water for each gram of chromium trioxide.

4. **5 M PHOSPHOROUS ACID SOLUTION.** Each milliliter of solution should contain 0.41 gram of anhydrous phosphorous acid. The authors have prepared phosphorous acid of required quality by adding 1 part of phosphorus trichloride in small amounts to 1.5 parts of continuously cooled water. After the reaction is complete, water and hydrogen chloride are removed by boiling, first to 150° C. under atmospheric pressure, and then to 180° C. under reduced pressure.

5. **5 M POTASSIUM CARBONATE SOLUTION (0.69 gram per ml.).** It may be necessary to subtract a small blank for this reagent, used in the analysis of urine.

6. **0.5 M POTASSIUM CARBONATE SOLUTION.**

7. **0.1 M SULFUROUS ACID SOLUTION.** Place 11 grams of

sodium bisulfite in a distilling flask and put the condenser stem of the apparatus in 1000 ml. of water. Add sufficient dilute sulfuric acid through the entry tube to decompose the sodium bisulfite and briefly distill. This solution decomposes readily.

8. 0.2 M POTASSIUM PERMANGANATE SOLUTION, 0.0316 gram of potassium permanganate per ml. of solution.

9. 85 PER CENT PHOSPHORIC ACID.

10. 1.5 M SODIUM NITRITE SOLUTION, 0.104 gram per ml. of solution.

11. 5 M UREA SOLUTION, 0.3 gram per ml. of solution.

12. ONE PER CENT STARCH SOLUTION. Add 10 grams of soluble starch in the form of a paste and 10 mg. of powdered mercuric iodide to 1 liter of boiling water and then boil the solution 5 minutes.

13. 0.30 M POTASSIUM IODIDE SOLUTION, 0.0498 gram of potassium iodide per ml. of solution. This solution should give no color with starch when cooled to 0° C.

14. 0.0002, 0.001, AND 0.01 N SODIUM THIOSULFATE SOLUTIONS. Dilutions are made of 0.1 N sodium thiosulfate (24.82 grams of the hydrated salt per liter), and 0.5 ml. of concentrated ammonium hydroxide is added per liter as a preservative. Solutions should be kept in a dark and cool place and standardized each week against standard dilutions of 0.1 N potassium binoiodate (32.51 grams per liter). If the solution employed in the standardization of the 0.0002 N thiosulfate is approximately 2 ml. in volume; 1 M in sodium chloride; 0.2 M in phosphoric acid, and 0.005 M in potassium iodide; and if 0.2 microequivalent of iodate is titrated, then the error of standardization will be small.

Procedure

OXIDATION. The procedure as given below is for amounts of biological materials of normal iodine content, as determined for this region. The biological specimen, which should be in a homogeneous state, is mixed in a distillation flask with an amount of chromium trioxide solution which provides chromium trioxide in excess of the amount required for complete oxidation. Since the reaction is vigorous, the sulfuric acid must be added in small portions at first and the specimen must be cooled or permitted to stand between additions.

BLOOD. To 25 ml. of blood in a 1200-ml. flask add 38 ml. of chromium trioxide solution. Then add 15 ml. of sulfuric acid slowly while the flask is being rotated. After the mixture no longer boils vigorously, repeat the operation. Finally add 160 ml. of sulfuric acid.

URINE. Add 1 ml. of 5 M potassium carbonate solution to 100 ml. of normal urine. Place 2 antibumps in the flask and concentrate the urine to 10 ml. In order to avoid loss by foaming evaporate slowly, or boil in the presence of a jet of compressed air. Add 10 ml. of chromium trioxide solution and 50 ml. of sulfuric acid.

DRIED FOOD. Dried food (or other specimens of low iodine content) containing at least 2 micrograms of iodine is oxidized according to the procedure of von Kolnitz and Remington (7). The basic absorbing solution and washings are boiled down to 10 ml. and treated with 10 ml. of chromium trioxide solution and 50 ml. of sulfuric acid.

In the analysis of 5 grams of dried and powdered feces, 0.1 to 0.2 gram of dried and powdered thyroid, or 25 ml. of milk, 30, 5, and 30 ml. of chromium trioxide solution are used, respectively. In general, 5 ml. of sulfuric acid are employed for each milliliter of the 10 M chromium trioxide solution; however, a minimum of 50 ml. of sulfuric acid is used.

After the addition of the sulfuric acid the mixture is heated rapidly in a hood to 220° C. and maintained at that temperature for 5 minutes. This heating suffices to decompose the excess chromium trioxide to a concentration smaller than 30 milliequivalents per 100 ml. of sulfuric acid.

DISTILLATION. When the flask has cooled to below 100° C., a volume of water equivalent to 25 ml. in excess of the sulfuric acid employed is added. Two antibumps are then added and the mixture is stirred thoroughly by rotating at a 45° angle. The flask is then connected to the apparatus, which has been first thoroughly washed. An Erlenmeyer flask containing an antibump, 0.5 ml. of 0.5 M potassium carbonate, and 0.5 ml. of 0.1 M sulfurous acid is placed under the condenser stem so that the tip dips into the solution. The flask is then heated and as soon as the distillation begins, 5 ml. of 5 M phosphorous acid are added through the entry tube for each 100 ml. of sulfuric acid in the flask. The distillation is made at approximately the rate of 100 ml. per 15 or 20 minutes. A volume equivalent to 25 ml.

plus one-half the volume of acid, but a maximum of 100 ml., is distilled. This procedure has been tested for amounts of sulfuric acid from 50 to 400 ml. The distillate is boiled down to from 3 to 5 ml. The samples are then quantitatively transferred to 25-ml. Erlenmeyer flasks, and boiled to a 1-ml. volume.

PERMANGANATE OXIDATION. Place the sample in a shallow boiling water bath. Add 0.2 M potassium permanganate, from the pipet of a dropping bottle, directly into the solution until a permanent purple coloration results. One drop (0.03 ml.), or two, is usually sufficient. After adding the permanganate, rotate the solution gently upon the sides of the flask and heat the samples for 2 minutes. Then add 2 drops (0.06 ml.) of 85 per cent phosphoric acid. No decolorization of the permanganate should occur. After 2 minutes add 1.5 M sodium nitrite solution drop by drop directly until all manganese dioxide and excess permanganate are reduced. Add 1 drop of nitrite solution in excess and thoroughly rotate the solution upon the sides of the flask, in order to reduce any manganese dioxide particles there. Finally, after the solution has stood for 2 minutes, add 1 drop of 5 M urea. Rotate the solution thoroughly upon the walls of the flask, and permit the sample to stand 4 minutes longer in the water bath. Cool the sample to room temperature (20° to 30° C.) before titration.

THE TITRATION. One drop (0.03 ml.) of 0.3 M potassium iodide is added to the samples. One drop of starch solution is then added and the liberated iodine is titrated with 0.0002 N or 0.001 N thiosulfate solution.

The distillation, permanganate oxidation, and titration procedures which have been described should be slightly modified for specimens containing more than 20 micrograms of iodine. The distillate should be collected in 2 ml. each of 0.5 M potassium carbonate and 0.1 M sulfurous acid. The permanganate oxidation should be made in a 5-ml. volume with appropriately larger quantities of reagents. At the titration as much as 1 ml. of potassium iodide solution may be added. The starch solution should be added just before the end point.

TABLE I. DETERMINATION OF IODINE IN BIOLOGICAL SUBSTANCES

Specimen	Iodine Content	Iodine Added as Iodophen		Iodine Recovered	%
		Micrograms			
Reagents for 25 ml. of blood	0.06
	0.05
25 ml. of blood	0.50	1	1.49	96.0	98.0
	0.52	1	1.51	98.0	99.0
	0.53	20	20.3	99.0	99.0
	0.56	20	20.4	99.0	99.0
0.1 gram of thyroid	0.53	400	399.0	99.6	100.4
		400	402.0	100.4	
0.2 gram of thyroid	63.8
	64.7
25 ml. of milk	129.8
	131.2
2.5 grams of feces	3.58	20	23.3	98	99
	3.66	20	23.4	98	99
5.0 grams of feces	3.62
	22.8
100 ml. of urine	23.5
	46.3
1 ml. of 0.0002 N thiosulfate	46.8
	4.39	20	24.5	100.0	101.0
1 ml. of 0.001 N thiosulfate	4.56	20	24.7	100.0	101.0
	4.48	400	398.0	98.4	98.9
1 ml. of 0.01 N thiosulfate		400	400.0	98.9	

Iodine factors for the standard thiosulfate solutions are as follows:

1 ml. of 0.0002 N thiosulfate	4.23 micrograms
1 ml. of 0.001 N thiosulfate	21.16 micrograms
1 ml. of 0.01 N thiosulfate	211.6 micrograms

Application of the Method

The method has been tested on several types of biological specimens. To demonstrate the percentage of recovery, the determinations shown in Table I were made. Standard solutions of recrystallized iodophen (tetraiodophenolphthalein) were added to the fluid specimens.

These, as well as other results obtained, indicate that rigorous application of the method as described should make possible determinations with a precision of within 5 per cent of amounts of iodine from 2 to 400 micrograms. Below 2 micrograms the possible error of titration of from 0.02 to 0.04 microgram must be considered. This source of error, as well as others, makes impossible the limitation of error to within even 10 per cent in determining amounts of iodine below 0.5 microgram.

With four complete apparatus available, four analyses of blood have been made easily by one person in 2.5 hours.

Different investigators have employed varying methods of determining the normal iodine content of human blood (10). Considerable variation of the average values obtained, and of the range, have resulted (2). This study (9) indicates that certain of the higher ranges may be due to the use of chlorine as an oxidizing agent and to the presence of iodine in the potassium hydroxide employed. Nevertheless, employment of this chromium trioxide procedure has yielded consistently since August, 1935, human blood values in this region of around 4 micrograms per 100 ml.

Summary

Peculiarities of the starch-iodine reaction necessitate the use of reagents of known iodine content.

Methods which have been devised permit the preparation of reagents of desirable purity with respect to small amounts of iodine.

The permanganate procedure yields results which are

more accurate than those obtained by the use of bromine or chlorine.

A distillation procedure, using a special apparatus, renders vacuum-steam distillation and aeration-distillation unnecessary.

Results obtained indicate that a precision of 5 per cent is attainable with amounts of iodine from 2 to 400 micrograms.

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Estimation of Copper, Zinc, and Cobalt (with Nickel) in Soil Extracts

Dithizoné Methods Particularly Adapted to Examination of Soils

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THE present paper is chiefly devoted to isolation and measurement of small amounts of copper, zinc, and cobalt, such as are usually found in soils, using an elaboration of dithizone methods. The procedures are thought to be generally applicable to extraction of these metals from almost any dilute aqueous solution, and to measurement of the separated metals.

Preliminary Work

In addition to the methods for preparing apparatus and reagents previously described (5), the following may be added:

After the glassware has been cleaned by usual methods, rinse with dilute (1 to 3) hydrofluoric acid to remove the siliceous film which sometimes adheres very firmly to glass after it has held soil or rock extract, which usually contains soluble silica. After the hydrofluoric acid rinse, wash immediately with pure water. To test for freedom from metals extractable by dithizone, place in the vessel about 50 cc. of the 0.02 *N* ammonia wash, described below, 5 cc. of chloroform, and a few drops of dithizone solution and shake vigorously. The chloroform should remain colorless or greenish. If it is colored, further purification is necessary.

Stopcocks are lubricated by a paste of flake graphite in glycerol. Very pure dithizone, which is necessary for precise work, may be prepared by the method of the Association of Official Agricultural Chemists (1). The procedure described by Wilkins *et al.* (13) provides a somewhat less pure dithizone.

Aqueous solutions of reagents containing objectionable metals, such as copper, zinc, and lead, may be freed of them by making slightly alkaline with ammonia, then shaking out repeatedly with dithizone in chloroform till no more metal is extracted. If dithizone in the aqueous solution is objectionable, it may be removed by shaking out repeatedly with chloroform. In nearly all cases carbon tetrachloride may be used instead of chloroform, though it seems to have more tendency to form emulsions than chloroform, and it is perhaps preferable to chloroform for extracting metals from acid solutions. Ordinary concentrated hydrochloric acid when distilled carries some zinc over with it. To purify it by distillation it should be diluted with water, so that it contains not over 20 per cent of hydrochloric acid, and distilled through all-Pyrex apparatus. Ammonia may be purified by distillation without dilution.

Additional Procedures

Reagents and apparatus are rarely quite free of zinc; therefore it is important to make frequent blank tests which will permit a proper correction. Because the blank frequently amounts to a considerable portion of the total found and is variable in amount, the final result may have considerable plus or minus percentage errors. Perhaps this should be expected when working with the very small quantities of metals, 1 to 20 micrograms (gamma), here considered.

In extracting a solute from solution A by means of an immiscible solvent B, there is nearly always a partition of the

solute between the two solvents. In consequence of this it is necessary to extract solution A by means of solution B perhaps two to five times in succession in order to effect nearly complete separation.

A number of metals may be separated by extraction with dithizone from suitably acidified solutions. Such extractions require much more vigorous and longer continued agitation of the two liquids together than do extractions from slightly alkaline solutions. Detailed procedure for each case may readily be developed from the experience of the analyst.

Exact separations usually require washing each of the two separated liquids with a small portion of the other solvent, adding this wash to the main portion of the same solvent. Thus the chloroform extract is washed with water and the aqueous solution with chloroform. In drawing off the chloroform extract, one must decide whether to leave a little of the chloroform with the aqueous solution or run a little of the aqueous solution out with the chloroform extract. The decision must depend upon the particular separation in question.

Excess dithizone usually must be washed out of the chloroform solution of the metal dithizonates being extracted, by two or more successive washings with the 0.02 *N* ammonia wash. A series of separatory funnels containing the wash solution is to be used for the successive washings. To avoid loss of metal in these washings, it is well to use the last dithizone extract to collect any metal dithizonates from the successive wash solutions by washing each of them with it and finally adding it to the main portion of the washed extract. This requires less chloroform and collects all the extract. Considerable experience with the use of dithizone for separating or measuring small amounts of metals must be acquired before very good results should be expected.

HANDLING OF EMULSIONS. Persistent emulsions may be broken by filtering through a cotton plug in the neck of a small funnel, or by drawing off the clear portion of the chloroform, adding fresh chloroform to the emulsion, agitating gently, letting it separate, and again drawing off the clear portion. This is repeated if necessary to recover all of the dithizonate from the emulsion.

A similar procedure may be used to avoid long waiting for the two liquids to separate sharply, even though there is not much emulsion present. Frequently small droplets of the chloroform are slow in settling out of the aqueous phase.

PRESERVATION OF DITHIZONE EXTRACT. The dithizone compounds with metals are slowly decomposed by light and air; therefore they should be kept in the dark, well stoppered, until they are titrated to determine the amount of metal present. This should not be delayed more than a few hours.

Estimation of Isolated Metals

The previous paper (5) describes various methods for estimating the amount of zinc in the chloroform dithizone extracts by color comparisons, and also gives the method for titrating the zinc dithizonate with bromine.

Recent refinements of the bromine titration procedure have made it sensitive enough for measuring all but amounts of 2 gamma or less of zinc, which are better estimated by color comparison.

PREPARATION OF BROMINE SOLUTION. Dissolve 1 cc. of pure bromine in 100 cc. of carbon tetrachloride for a stock solution to be preserved in a glass-stoppered bottle away from light. For the working solution dissolve 1 cc. of the stock solution in 200 cc. of carbon tetrachloride and keep in a dark bottle connected with a 2-cc. buret, so that the buret may be filled to zero automatically by suction at the top of the buret, not by pressure on the solution of bromine in carbon tetrachloride. Avoid entrance of moisture or air as much as possible into the bromine solution. Except when in use, the bromine solution should be kept in a dark glass-stoppered bottle away from light and air. This solution is not

constant in oxidizing power, slowly becoming weaker, and therefore should be checked against a known amount of zinc or other metallic dithizonate every day or two. A solution of 7.4 mg. of arsenious oxide dissolved by heating with 0.2 gram of sodium bicarbonate and diluted to 100 cc. provides a good standard for measuring the strength of the bromine solution. One cubic centimeter of the arsenious solution reduces the bromine equivalent to very nearly 5 gamma of zinc as the dithizonate. When fresh, 1 cc. of bromine solution is equivalent to 7 to 9 gamma of zinc as dithizonate. This bromine solution is nearly equal to 0.001 *N* thiosulfate.

TITRATION. Place the chloroform solution of zinc dithizonate to be titrated in a 60-cc. narrow-mouthed, glass-stoppered bottle, and add the bromine solution slowly with frequent shaking of the bottle until the red color fades to colorless, or yellowish when much zinc is present. If the amount of bromine required is approximately known it may all be added at once, quickly. Several minutes should be allowed for completion of the reaction. The end point is not distinct; therefore add some excess of bromine, and after 5 minutes about 1 cc. of the 20 per cent potassium iodide in water, followed by a little starch solution and 5 cc. of water containing 1 per cent sodium bicarbonate. The excess bromine liberates iodine which is titrated to colorless with 0.001 *N* thiosulfate. One per cent of sodium bicarbonate added to the boiled water used to dissolve the sodium thiosulfate keeps it from losing strength for several days. This method is applicable to amounts of zinc from 1 to 30 gamma; for smaller amounts the color comparison method is better (5). If insufficient bromine has been added, no blue will appear on adding iodide and starch. In this case, add more bromine till blue, shake a minute, then complete the titration with the thiosulfate. More reliable results are obtained if excess bromine is added before back-titration is begun.

Lindner (8) has measured the zinc in the dithizone complex by adding an excess of ceric sulfate and titrating back with ferrous sulfate, using *o*-phenanthroline ferrous complex as indicator. He reports excellent results, not yet offered for publication.

Copper, lead, cobalt, cadmium, and some other metals may be extracted by dithizone and amounts measured by titration with bromine much as zinc is estimated. In order to determine the equivalence of the bromine solution with respect to the particular metal in question, a 10-gamma portion of the metal is extracted by the appropriate dithizone procedure and titrated with the bromine solution.

Isolation of Copper, Zinc, and Cobalt

The following procedures have been used for removal and isolation of 1 to 50 gamma of copper, zinc, and cobalt from soil extracts. (If nickel is present, an indefinite amount will be included with the cobalt.) The procedures should be equally applicable to any dilute aqueous solution which does not contain the noble metals or mercury. These extracts were made by use of a normal solution of potassium chloride containing enough acetic acid to make the pH about 3.6 with a total acidity about 0.04 *N*. The solutions contain some iron and manganese. To prevent them from interfering, 2 cc. of a 10 per cent solution of ammonium citrate are added to 400 cc. of the soil extract before beginning the separations.

If a solution contains many of the metals which form dithizonates, the isolation of any single one may be very complicated. However, in soil extracts there are likely to be only a few present in appreciable amounts, so that the difficulties are not great.

ISOLATION OF COPPER. Copper is removed from the acid solutions by repeated extraction with dithizone in chloroform. Bismuth, if present, will be included with the copper. The solution may have a pH of 1 to 4. After copper and bismuth have been separated from the original solution, wash the extract with 20 cc. of 0.01 *N* hydrochloric acid to remove any zinc, which is added to the main solution, then wash the copper solution free of excess dithizone by the dilute ammonia wash. Extract copper and bismuth from the chloroform by shaking with 1 per cent nitric acid. Neutralize the acid solution with sodium or potassium hydroxide, add enough tartaric acid to make the solution 0.5 *N*, and again extract the mixture with dithizone as at first.

The copper again combines with dithizone, while very little of the bismuth does.

Bismuth may be separated from copper by extracting copper with dithizone from a solution of both in 0.5 *N* hydrochloric acid. Bismuth remains in the acid aqueous solution. However, it is difficult to extract the copper completely from 0.5 *N* hydrochloric acid. Several successive extractions are necessary. These separations may not be perfect. They have not been critically examined by the writer, since no evidence of bismuth in the soils studied has been found. A somewhat different procedure has been described by Stolze (11).

The copper extract is washed free of dithizone by 0.02 *N* ammonia, then drawn off into a small bottle for estimation of copper by the bromine titration method, described above.

TABLE I. SEPARATION OF KNOWN AMOUNTS OF COPPER, COBALT, AND ZINC BY THE DITHIZONE METHOD

Expt. No.	Taken		Found		Zn	Treatments
	Cu	Co	Cu	Co		
42	10	..	10	3 extractions from 200 cc. of KCl solvent
43	..	10	..	10	1.8	5 extractions with 0.01 <i>N</i> HCl
45	10	(8.6 3 extractions with 0.01 <i>N</i> HCl 0.7 4th extraction with 0.01 <i>N</i> HCl
47	10	..	10	No separations
48	10	10	10	10.5	9.4	7.2 4 extractions from 300 cc. of KCl solvent
49	10	10	10	11.2	10.0	9.1 4 extractions from 300 cc. of KCl solvent
50	Blank on 200 cc. of KCl solvent		0.8	0.6	2.1	3 extractions for each
51	10	10	10	12.3	10.6	7.9 From 200 cc. of KCl solvent
52	..	10	..	1.3	10	.. From 200 cc. of KCl solvent
53	10	10.5	..	10
54	..	10	..	2.6	10	1.4 Direct, no separation
55	10	1.0	1.1	10 3 extractions on each from 200 cc. of KCl solvent
57	10	..	10.6	..
58	10	8.7 Simple extraction, no separations
59	..	10	10.6	..
60	..	10	10.0	..
12	50	..	10	9.8 3 extractions by 0.05 <i>N</i> HCl
13	..	50	10	10.8 3 extractions by 0.01 <i>N</i> HCl
15	10	50	..	12.1 2 extractions by 0.05 <i>N</i> HCl
18	50	3.1 2 extractions by 0.05 <i>N</i> HCl
19	..	50	3.1 2 extractions by 0.05 <i>N</i> HCl
39	..	10	9.9	.. By choline test
40	..	10 nickel	..	7 nickel By nitroaminoguanidine
41	..	30 nickel	..	26 nickel By nitroaminoguanidine

SEPARATION OF ZINC AND COBALT. After removal of copper and bismuth, neutralize the aqueous solution to pH 7 to 9 (phenol red) and extract zinc and other metals which may accompany it (such as lead, cobalt, nickel, and cadmium) with dithizone and chloroform. Wash free of excess dithizone with ammonia wash. Remove the zinc, including lead and cadmium, if present, from the cobalt by shaking out three or more times successively with 20- to 30-cc. portions of 0.01 *N* hydrochloric acid. If there is much more cobalt than zinc in the solution being analyzed, the separation above described is imperfect, and some cobalt is extracted with the zinc by the 0.01 *N* hydrochloric acid. To complete the separation repeat the process once or twice, by again making the acid extract alkaline, recombining with dithizone as at first, and again extracting the zinc with 0.01 *N* hydrochloric acid. Zinc, lead, and cadmium enter the acid solution, while the cobalt and most of the nickel remain in the chloroform. Wash free of excess dithizone with ammonia wash, and draw off the cobalt solution, including nickel, for estimation of cobalt by bromine titration. (The titrated solution is brownish if much cobalt is present.)

The acid aqueous solution contains the zinc and perhaps lead and cadmium. Bring the pH to 7 to 9 again, extract the zinc with dithizone in chloroform, wash free of excess dithizone, and draw off the zinc solution for titration with bromine. Since lead and cadmium have not been encountered in the soil extracts examined, little study of a means of separating them has been made by the writer.

In case lead is present, addition of 1 per cent of potassium cyanide to the solution will prevent zinc and cadmium from combining with dithizone, so that the lead alone is extracted. The details of procedure are given by Clifford and Wichmann (2), Hubbard (6), and others (5, references).

Sandell (10) estimates zinc in mixture with lead by titrating with dithizone in presence of thiosulfate at pH 4.1. This procedure has not been examined by the writer.

Cadmium is neatly and easily separated from zinc by dithizone in 5 per cent sodium hydroxide (4, Fischer's method); the zinc remains in the alkaline aqueous solution from which it may be extracted by dithizone as usual after neutralizing the excess of sodium hydroxide. Cadmium present as dithizonate in the chloroform extract may be estimated the same as zinc, by titration with bromine as described above.

In using this scheme for separating these metals, if both copper and cobalt are present, as they usually are, the copper must be removed from the solution before it is made alkaline, because both copper and cobalt are extracted from alkaline solutions by dithizone and are not separated by shaking out with acid. But if it is desired to determine the zinc only in a mixture of the three metals, all may be extracted at once from alkaline solution. Then the zinc is removed from this extract by shaking out with 0.01 *N* hydrochloric acid as above described, leaving the copper and cobalt together in the chloroform, the acid solution containing the zinc is made alkaline, and the zinc is again extracted by dithizone as usual.

Attempts to separate nickel from cobalt by extracting the chloroform solution of the dithizonates of both with acid were not successful. Hydrochloric acid 0.01 to 0.5 *N* was used. The stronger the acid the greater was the amount of nickel and cobalt extracted, but even 4 *N* hydrochloric acid decomposed cobalt dithizonate only slowly and incompletely. Probably 0.5 *N* hydrochloric acid will extract all the nickel from such a mixture together with much of the cobalt. Then, if both are extracted by dithizone from the acid aqueous extract after it has been made alkaline, the dithizonates can be again extracted with 0.5 *N* hydrochloric acid and thus more of the nickel isolated. Repetition of this tedious procedure might effect almost complete separation of the two metals.

SEPARATION AND ESTIMATION OF COBALT AND NICKEL. No satisfactory means of separating these metals by dithizone has been found suitable for the small amounts present in the soil extracts examined. The color methods here described afford a partial solution of the problem.

A recent paper by Fischer (3) describes determination of numerous metals by dithizone but omits separation of nickel and cobalt. The nitroso R salt test of Van Klooster (12) is not satisfactory, on account of lack of sensitivity and because the color of the reagent itself tends to obscure the color of its cobalt compound.

The choline test (Jacobs and Hoffman, 7) has been found specific for cobalt and not interfered with by small amounts of nickel, zinc, or copper. It may be made by adding to the neutral solution (about 2 cc.) 1 cc. of 1 per cent choline hydrochloride and 2 cc. of a 2 per cent solution of potassium ferrocyanide. Appearance of an emerald-green color indicates cobalt.

The nitroaminoguanidine test (Phillips and Williams, 9), which seems to be specific for nickel, may be made by adding to 5 to 10 cc. of the solution 0.5 cc. of the reagent (1 per cent in dilute nitric acid) and 1 to 2 cc. of *N* sodium hydroxide, or enough to make alkaline. Presence of 5 gamma of nickel in 10-cc. volume is indicated by a clear blue-green color, not interfered with by several times as much cobalt. (A cobalt chloride marked c. p. contained enough nickel to give the test distinctly in 30 gamma of cobalt.)

For lack of a better method, the following is proposed for estimating the amount of nickel and cobalt in the mixture after the dithizonates have been titrated with bromine: Empty the titrated mixture into an evaporating dish, and evaporate to dryness on the steam bath. Add hydrochloric and nitric acids and evaporate to dryness once or twice to remove organic matter. Then evaporate once with hydrochloric acid to remove nitrates and take up in a little dilute hydrochloric acid. Divide the solution and estimate cobalt in one part by the choline test (7) and nickel in the other part by the nitroaminoguanidine test (9).

This procedure is proposed for use where the amounts of the metals are 5 to 10 gamma, too little for separation by the usual chemical methods.

Results

Results obtained in separation of approximately known amounts of the metals are given in Table I.

On account of impurities in the metals used as standards and in reagents, of imperfection in separations, of smallness of the amounts of metals taken for analysis, and of large volumes of solution involved, considerable variations in amounts of metals found may be expected. However, since the amounts concerned are all stated as micrograms (1 microgram = 1 gamma = 0.001 milligram), most of the results are fairly good. Repeated trials showed that the cobalt solution

used contained about 0.6 gamma of zinc in 1 cc. which was calculated to contain 10 gamma of cobalt (experiment 19). The copper solution used in these experiments contained zinc. Estimation of the amounts in each case except 39, 40, and 41 was made by bromine titration of the dithizone extracts. The separations were made by decomposition of the dithizone extracts with dilute hydrochloric acid of various normalities as indicated in Table I. Usually 20 to 30 cc. of the acid were used for each extraction. In experiment 39 cobalt was estimated by the choline test on the dithizone extract after it had been titrated with bromine which indicated 10 gamma of cobalt.

TABLE II. COPPER, COBALT, AND ZINC
Extracted from soils by acidified potassium chloride solvent

Soil No.	Copper P. p. m.	Cobalt P. p. m.	Zinc P. p. m.
59	1.1	0.8	7.8
64	2.1	5.3	4.3
78	1.6	4.0	4.5
89	0.5	1.2	5.3
112	0	0.4	1.2
122	0.5	0.4	2.2
136, top	1.2	2.9	5.6
136, subsoil	0	0.2	1.4
144	0	0.4	1.3

The nickel found by the nitroaminoguanidine test in experiments 40 and 41, after the dithizone extraction, is low for reasons not known. There appears to be a tendency for some cobalt and zinc to be included with copper. Quantitatively these figures are not very good, but they show the degree of accuracy that may be expected.

Since the purpose of this study was chiefly to find a means of making reliable estimations of zinc in soil extracts, no great effort was made to work out procedures capable of giving more exact results for other metals. In absence of interfering substances it seems that 10 to 30 gamma of each of these metals may be easily extracted from aqueous solutions by dithizone and estimated by titration with bromine, with an accuracy of ± 10 per cent. Where separations have

been made by repeated extractions, results are less accurate because of imperfection in methods and uncertainty of amount of the blank.

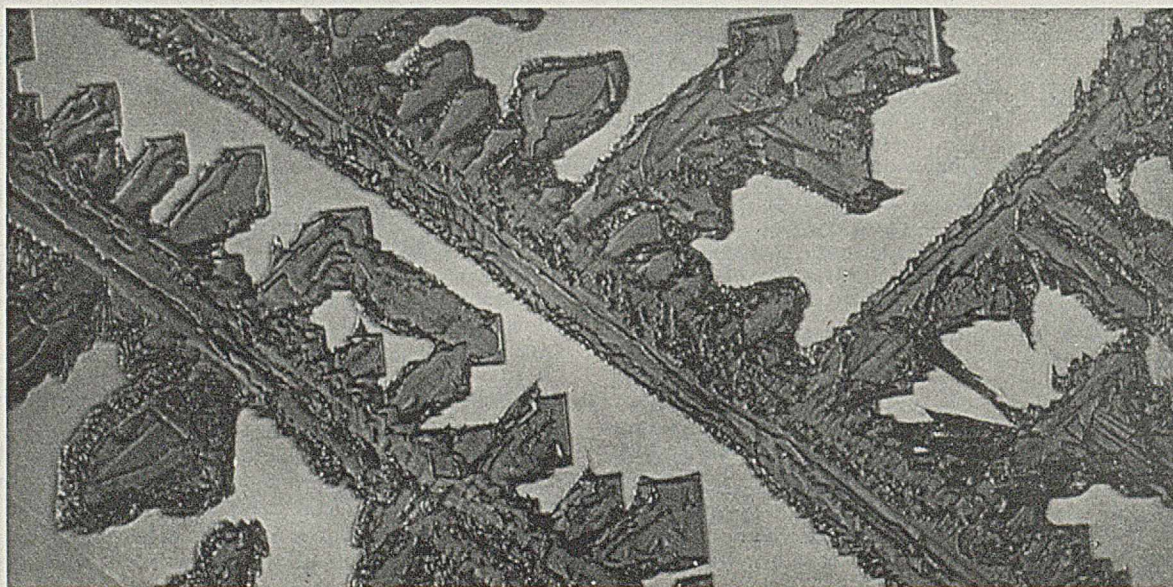
In Table II results obtained in analysis of soil extracts by these methods are given. These soil extracts were made with a molal solution of potassium chloride to which had been added enough acetic acid and ammonia to buffer it and make the pH 3.6 and the titratable acidity equal to 0.04 N. In these soil extracts other metals which may combine with dithizone, under the conditions described, were not present in appreciable amounts, except iron and manganese. Interference from those was prevented by addition of ammonium citrate.

Most quantities in Table II are averages of two or more separate determinations. There is some variation in the amount obtained from any soil by replicate extractions with potassium chloride solvent. Table II is included to illustrate applicability of the dithizone methods to examination of soil extracts, not to show what may be found in soils. It is planned to report upon soil zinc in another paper which will include much detail in respect to numerous soils.

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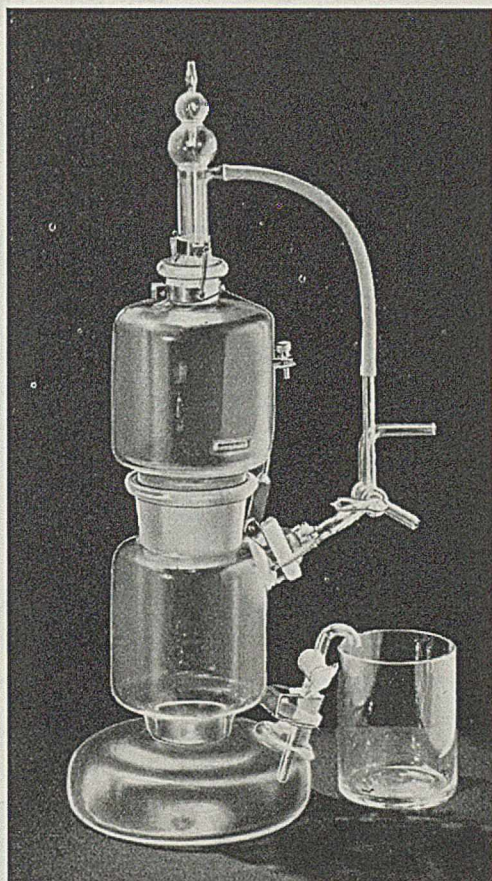
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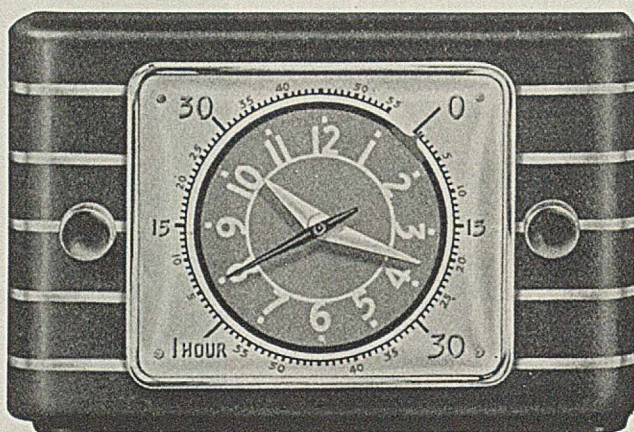
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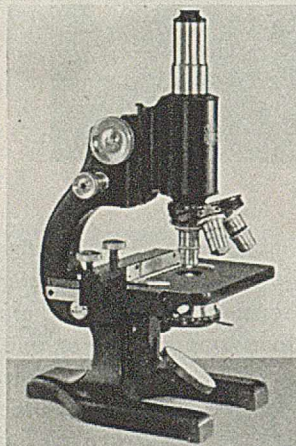
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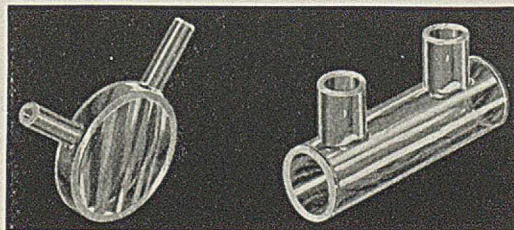
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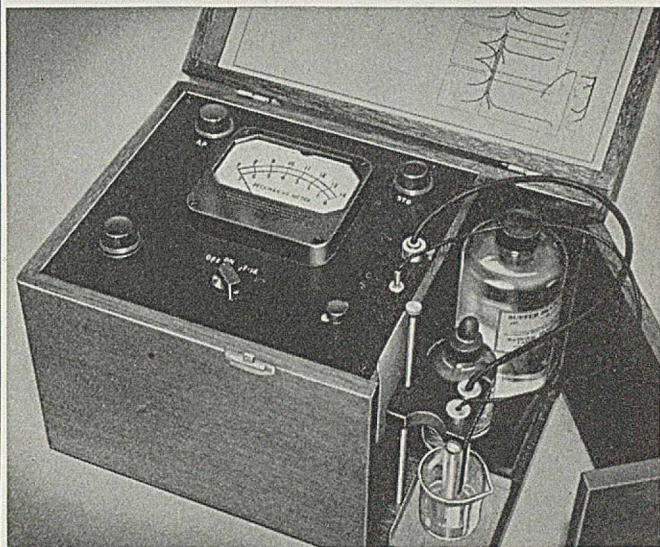
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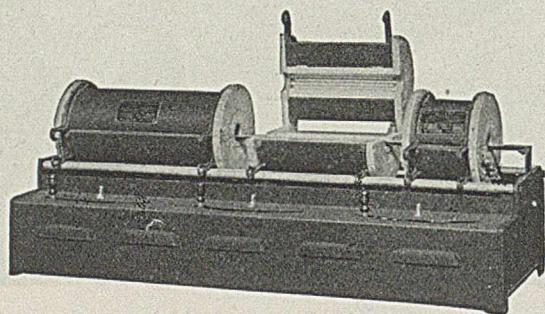
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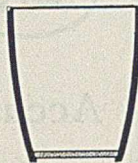
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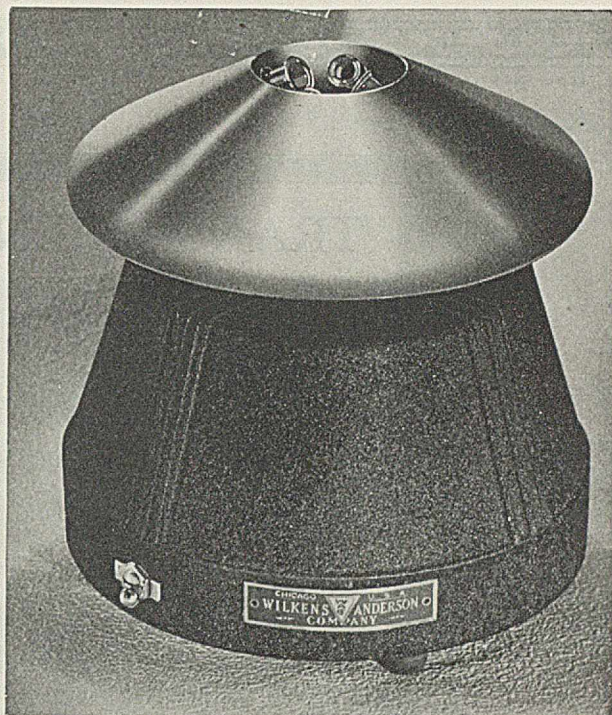
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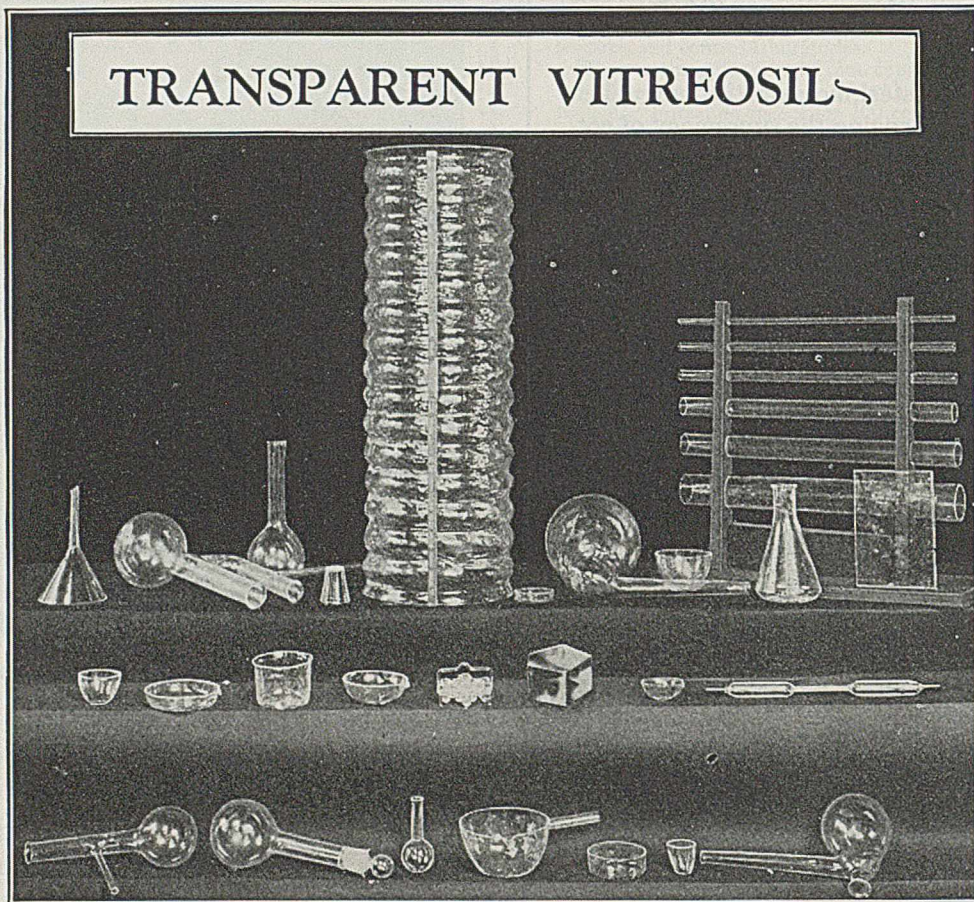


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