SCIENTIFIC SECTION

ALKALOIDAL REAGENTS. VII. THE DETECTION OF THALLIUM.*

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In connection with our studies on thallium the need arose for rapid, sensitive, specific methods of qualitative detection and of quantitative determination, in tissues, plants, soils and various types of products.

Thallium forms two series of compounds, being monovalent and trivalent. In general the trivalent or thallic compounds are unstable, being reduced to the thallous products. Commercial material used for cosmetics, medicinal and rodenticidal purposes is almost entirely thallous thallium.

In the flame, thallium compounds dissociate, liberating Tl which produces a characteristic green color and spectrum. If this flame is allowed to strike on a cold surface, a brown mirror of Tl forms (73). In the Marsh apparatus the stain produced is similar to that produced by arsenic, but it gives a characteristic yellow color with iodine and is insoluble in ammonium sulphide (11). Spectroscopic studies of the emission spectra (67) show a number of characteristic lines, between 2552.9 Å. and 71170 Å. In the visible spectrum the line usually considered to be characteristic is at 5350.47 Å. Using the spectroscope, a number of qualitative investigations have been conducted (16, 25, 41, 43, 45, 51, 57, 72, 79, 82, 84, 99). The limit of sensitivity is reported to be 1 gamma, although Lamy claimed that he was able to detect 0.002 gamma of thallium by following the 5350 line. We have used the spectroscope in our investigations, but have also made a detailed search of the literature and a specific study of the more promising reactions with the view of developing quick methods to use when a spectroscope is not available. Our detailed results are given in Tables I and II.

TABLE I.—QUALITATIVE DETECTION OF THALLOUS THALLIUM.

No.	Name of Reagent.	Color in Solution.	Color of Precipitate.	Threshold, Mg. Tl/Cc.	Literature References.
1	H_2SO_4	None	None	....	.....
2	HNO_3	None	None	....	.....
3	Froehde	None	White	20	.....
4	Marquis	None	None	....	.....
5	Mayer	None	Curdy light yellow	0.2	.....
6	Dragendorff	None	Brown-black	2	.....
7	Wagner	None	Brown-black	2	.....
8	Picric acid	None	Yellow needles, prisms	20	(91)
9	$FeCl_3$	None	White needles	0.2	.....
10	$K_2Cr_2O_7$; NH_3	None	Orange-yellow cryst.	0.2	(91)
11	$K_4Fe(CN)_6$	None	Yellow	20	.....
12	" ; $Ca(CH_3COO)_2$	None	White	20	(1)
13	$KMnO_4$; HCl	Pink; none	Red-brown; white	0.2	(7, 17, 18, 42, 46, 58, 71, 104)

* Scientific Section, A. PH. A., Washington meeting, 1934.

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14	$PtCl_4$	None	Yellow octahedra	0.02	(3, 59, 80)
15	Schiebler	None	Yellow-white	2	.....
16	U Acetate	None; yellow	Yellow prisms	0.2	(19)
17	Mecke	None	None	....	.....
18	Millon	None	Yellow-white curd	0.2	.....
19	Na alizarin sulphonate, 0.5%	Dark blue	Blue-yellow	20	(40)
20	Alkanna; NH_3	Blue	None	....	(32)
21	Al	None	None	....	(59)
22	Al_2O_3	None	White prisms	0.2	(42)
23	$SbCl_3$; KI; dilute	None	Orange-yellow	0.2	(27)
24	K Antimonyl tartrate	None	White prisms	20	.....
25	Na_3AsS_3	None	None	....	(20)
26	As_2S_3; H_2S	None	Gray-black	0.2	.....
27	Benzidine	Blue	Blue	20	(29, 41)
28	Na benzoate	None	None	....	.....
29	$BiCl_3$	None	White	0.2	.....
30	Br; NH_3	None	White	0.2	(12, 89)
31	HBr	None	Pale yellow	2	(26, 59)
32	$NaBrO_3$ or $Mg(BrO_3)_2$	None	White	20	(58, 80, 89, 103, 106)
33	$CdCl_2$	None	White	0.2	.....
34	$Ce(SO_4)_2$,; $N/10$ HCl	Pale yellow	None	....	(6, 86, 103)
35	HCl	None	White	0.2	(3, 26, 59, 69)
36	$KClO_3$	None	None	....	.....
37	Citric acid	None	None	....	.....
38	$Na_3Co(NO_2)_6$, fresh 6%	None	Brick-red	0.2	(90, 95)
39	$Cr(NO_3)_3$ test paper	None	Green-yellow	20	(61)
40	K_2CrO_4	None	Yellow	0.2	(12, 14, 21, 41, 42, 55, 62, 63, 65, 66, 75, 81)
41	HCHO	None	Gray-white	20	.....
42	$K_3Fe(CN)_6$	Yellow	None	....	(4, 13, 33, 55, 80, 96, 97)
43	$AuBr_3$, fresh, hot	None	Yellow	20	.....
44	Hydroquinone	None	None	....	.....
45	HI	None	Yellow	0.2	(2, 3, 4, 11, 14, 22, 23, 26, 27, 31, 34–37, 41, 44, 47, 52–54, 58, 59, 67–71, 76, 85, 87, 88, 90, 97, 98, 102, 105)
46	NaIO	None	Dark brown	100	(101)
47	KIO_3; HCl	None	White plates	200	(5, 10, 24)
48	$Ir(NO_2)_3$	None	Yellow-white	....	(28)
49	NaF or NH_4F	None	Yellow-white	20	(106)
50	Mg	None	Black deposit	0.2	(90)
51	NH_4 Molybdate	None	White leaves	0.2	(38, 39, 91)
52	Sat. *a*-naphthol; dimethyl - *p* - phenylenediamine	None	None	....	(56)
53	Ozone	None	Brown	....	(83)
54	$PdCl_2$	None	Cinnamon-brown	0.2	.....

55	$AuPdCl_6$:HCl	None	Cinnamon-brown	0.2	(94)
56	Na_2HPO_4; alkaline soln.	None	White	20	(80)
57	KH_2PO_4:alkaline soln.	None	White	20	.....
58	Phosphomolybdic acid: HNO_3	None	Yellow	2	(38, 39, 74, 80)
59	Phosphotungstic acid	None	Milky white	0.2	.....
60	ReO_4:I_2	None	Dark plates	....	(49)
61	K_2ReBr_6	None	Violet	....	(48)
62	K_3ReCl_6	None	Dark brown	....	(48)
63	K_4ReCl_6	None	Brown-yellow	....	(48)
64	Saccharin	None	White rods, needles	20	(77)
65	Silicotungstic acid	None	Milky white	0.2	.....
66	$AgNO_3$; alkaline soln.	None	Dark brown	0.2	(100)
67	H_2S	None	Black	0.2	(15, 59, 64, 80, 82, 92)
68	S impurities in benzine; Tl ethylate	None	Orange	....	(50, 60)
69	S impurities in benzine; dimethyl-Tl-ethylate	None	Orange	....	(50, 60)
70	S impurities or CS_2; Tl acetyl-acetone	None	Orange	....	(30, 50)
71	S impurities or CS_2; Tl-yellow; CH_2Bz	None	Carmine	....	(30)
72	S impurities or CS_2; Tl-yellow; $AcCH_2Bz$	None	Cinnabar	....	(30)
73	CS_2; Tl-yellow; AcCH-MeBz	None	None	....	(30)
74	CS_2; Tl-yellow; $AcCH_2$-COCOOEt	None	None	....	(30)
75	CS_2; Tl-yellow; $BzCH_2$-COCOOEt	None	None	....	(30)
76	CS_2; Tl-yellow; EtO-$OCCOCH_2COOEt$	None	None	....	(30)
77	CS_2; Tl-yellow; $AcCH_2$-COOEt	None	Yellow	....	(30)
78	CS_2; Tl-yellow; $BzCH_2$-COOEt	None	Orange-red	....	(30)
79	CS_2; H_2S NH_3	None	Vermillion	0.2	(75)
80	KSCN	None	White prisms, needles	20	(91, 93)
81	$Na_2S_2O_3$	None	White prisms, rods	20	(9, 91)
82	Tartaric acid	None	White prisms	20	(91)
83	Tannic acid; NH_3	Red	Yellow-green	20	.....
84	TiO_2	None	None	....	.....
85	$SnCl_2$; KI	None	Dark yellow	0.2	(94)
86	$SnCl_2$; H_2S	None	Gray-white	0.2	(43)
87	Na Tungstate, 5%	None	White plates	20	(39)
88	Urea	None	None	....	.....
89	NH_4 metavanadate	None	None	....	.....
90	Zn	None	Black deposit	0.2	(59, 79, 80)

TABLE II.—QUALITATIVE DETECTION OF THALLIC THALLIUM.

No.	Name of Reagent.	Color in Solution.	Color of Precipitate.	Threshold, Mg. Tl/Cc.	Literature References.
1	H_2SO_4	None	None	..	.....
2	HNO_3	None	None	..	.....
3	Froehde	None	None	..	.....
4	Marquis	None	None	..	.....

5	Mayer	None	None	..	.....
6	Dragendorff	None	None	..	.....
7	Wagner	None	None	..	.....
8	Picric acid	None	None	..	.....
9	$FeCl_3$	None	None	..	.....
10	$K_2Cr_2O_7$	None	None	..	.....
11	$K_4Fe(CN)_6$	None	None	..	.....
12	$KMnO_4$	None	None	..	.....
13	$PtCl_4$	None	None	..	.....
14	Schiebler	None	None	..	.....
15	U Acetate	None	None	..	.....
16	Mecke	None	None	..	.....
17	Millon	None	None	..	.....
35	HCl	None	None	..	(3, 26, 59, 69)
45	HI	None	Yellow	20	(See Table I)
52	Sat. *a*-naphthol; dimethyl-*p*-phenylenediamine	Blue	None	20	(56)
64	Saccharin	None	None	..	.....
79	CS_2; H_2S; NH_3	None	Black	20	(75)
80	KSCN	None	Pale yellow	20	(91, 93)

It must be remembered that working conditions in various laboratories may influence the delicacy of response of these qualitative tests. We have suggested the approximate sensitivity of some of these reactions, solely as suggestion of their routine application, rather than as absolute limits for threshold reactions.

In making these tests, thallic sulphate and various thallous compounds were used (usually thallous sulphate). Since the atomic weight of thallium is 204.1 a normal solution would contain about twenty per cent of Tl. Our stock solutions were prepared as $N/10$ and $N/1000$ solutions with respect to Tl. When these solutions have given positive results, further dilutions have been prepared to determine the approximate threshold of sensitivity.

CONCLUSION.

Qualitative tests for thallium have been studied, using ninety reagents.

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LOCAL ANESTHETICS—PHENYL PROCAINE.*

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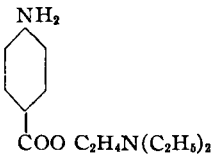
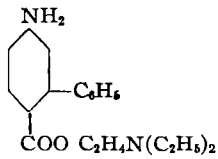
This investigation concerns the study of phenyl derivatives of procaine (I) and its analogues. The study was initiated by the comparatively greater activity and lesser toxicity of *o*-phenyl phenol over phenol. The substitution of a phenyl group on the benzene nucleus of procaine would yield, it was expected, a substance of greater potency and lesser toxicity than the parent substance. A summary of the biological activity of the various substances prepared is contained below.

The initial substance synthesized was phenyl procaine (II). The details of the preparation of (II) are stated in the experimental section. Essentially, the



(I)



(II)

synthesis employed was the preparation of 2-carboxy 5-amino diphenyl and the subsequent reaction of its sodium salt with β-diethylamino ethyl chloride. Phenyl procaine is an active anesthetic but due to such factors as precipitation upon the addi-

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