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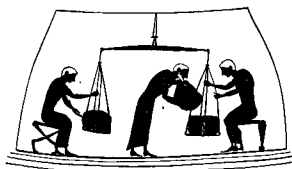
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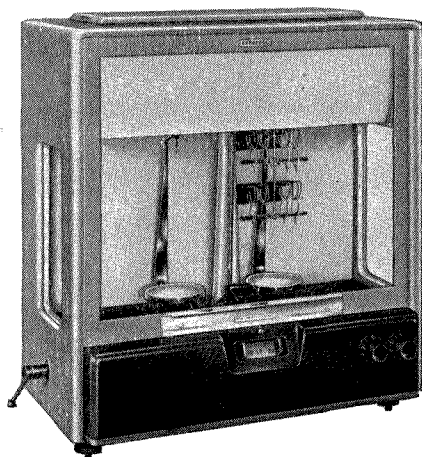
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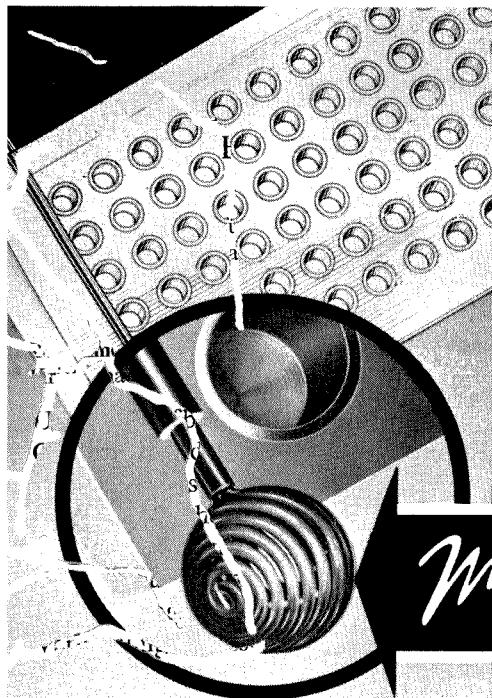
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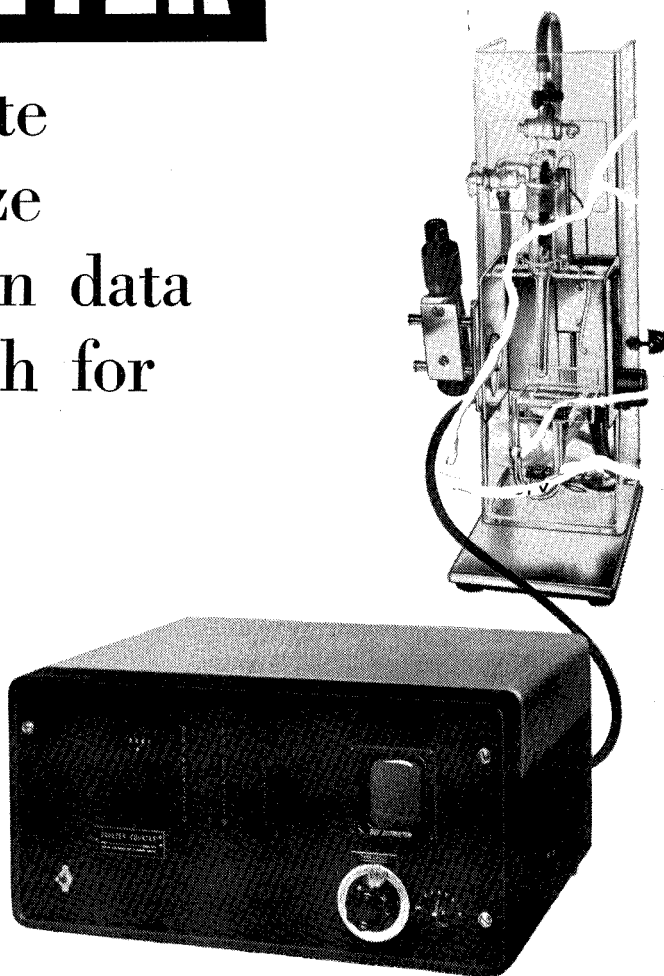
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BEITRÄGE ZUM AUFBAU EINIGER METALL-CARBAMATVERBINDUNGEN

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Zusammenfassung—Es werden von einigen Metall-Carbamatverbindungen die Bruttoformeln, der Kristallhabitus und die entsprechenden Debye-Scherrer-Diagramme gezeigt.

Um den Aufbau einiger der immer stärker in den Vordergrund der analytischen Chemie tretenden Metall-Carbamatverbindungen näher kennenzulernen, wurden aus reinen Metallsalzlösungen in den günstigsten pH-Bereichen¹⁻⁴ die entsprechenden metallorganischen Fällungen hergestellt.

Im folgenden wird eine Aufstellung über die chemische Zusammensetzung, wie sie auf Grund von Elementaranalysen gefunden wurde, über den Kristallhabitus, wie er nach langsamer Kristallisation aus den Chloroformlösungen der entsprechenden Verbindungen entstand, und über die Röntgenfeinstruktur dieser auskristallisierten Verbindungen gebracht.

Bei den hier vorliegenden Untersuchungen wurden nur Pulverdiagramme aufgenommen unter Verwendung einer Debye-Scherrer-Kammer mit einem Radius von 28,65 mm. Als Strahlung diente Kobalt-K α -Strahlung unter Vorschalten eines Eisenfilters. Die Aufnahme erfolgte symmetrisch zum einfallenden Strahl. Da keine Eichsubstanz mit aufgenommen wurde, sind die errechneten Netzebenenabstände nicht korrigiert. Die Aufspaltung in die Linien der K α_1 - und K α_2 -Strahlung wurde nicht beobachtet. Die Berechnung konnte daher mit der Wellenlänge K α = 1,786 kXE durchgeführt werden. Die Intensität der Linien wurde geschätzt, wobei die stärkste Interferenzlinie jeder Aufnahme mit "sehr, sehr stark" bezeichnet wurde. Die *Tafel I* gibt die Netzebenenabstände der reinen Fällungsmittel, *Tafel II* die Netzebenenabstände einiger aus Chloroform umkristallisierter Diäthylthiocarbamate und *Tafel III* die einiger ebenfalls aus Chloroform umkristallisierter Pyrrolidindithiocarbamate wieder. In den Tafeln sind die Interferenzlinien nicht nach fallendem Netzebenenabstand, sondern nach der Intensität geordnet. Es zeigt sich, daß alle Carbamate ein mehr oder weniger linienreiches Interferenzmuster ergeben und dass auch die Debye-Scherrer-Diagramme der Metallsalze sich untereinander sowie von den Fällungsmitteln unterscheiden. Die Kristallstruktur des Zinkdiäthylthiocarbamates wurde eingehend von Simonsen und Wah Ho⁵ untersucht.* Das vorliegende Debye-Scherrer-Diagramm stimmt im wesentlichen hinsichtlich der Intensitätsverteilung und Linienanzahl mit dem von den beiden vorher genannten Forschern

* Die aus Chloroform erhaltenen durchsichtigen Plättchen sind optisch einachsrig negativ. Die Strukturanalyse ergab, daß es sich hier um eine monoklin kristallisierende Verbindung handelt mit

$$\begin{aligned} a &= 10,02 \pm 0,02; \\ b &= 10,80 \pm 0,05; \\ c &= 16,00 \pm 0,02 \text{ \AA} \\ \beta &= 111. \end{aligned}$$

Die Raumgruppe hat 4 Elementarzellen.

TAFEL I. NETZEBENENABSTÄNDE DER REINEN FALLUNGSMITTEL

Intensität geschätzt	Natriumdiäthyl- dithiocarbamat	Ammoniumdiäthyl- dithiocarbamat	Natriumpyrroli- dindithiocarbamat	Ammonium- pyrrolidin- dithiocarbamat
	d kXE	d kXE	d kXE	d kXE
ststst	5,60 5,10	6,23	4,93 4,16	5,20 3,41
stst	4,21 2,71	6,58 4,24 4,08		2,82
st	3,40 3,19 2,93	7,58 5,20 5,00 3,23 3,14	3,27 3,11	7,83 3,89 3,20 •
m	2,44 1,89	4,66 4,45 3,68 3,56 2,81 2,74	3,89 2,53 2,21	5,60 4,17 2,86
s	3,07 2,10 1,79	3,42 3,05 2,96 2,50 2,45 2,20	3,60 3,42 2,45	3,62
ss	3,90 2,83 2,21 1,99	2,14 2,04 1,88 1,66	2,95 2,38 2,29 1,87 1,79	4,66 2,60 2,51 2,44
sss	2,59 2,05 1,67 1,41 1,40 1,35 1,33 1,30 1,28 1,23	3,90 2,88 2,29	2,09 2,01 1,97 1,72	2,36 2,20 1,92

ststst = sehr sehr stark

stst = sehr stark

st = stark

m = mittel

s = schwach

ss = sehr schwach

sss = sehr sehr schwach

TAFEL II. NETZEBENENABSTÄNDE EINIGER METALLDIÄTHYLDITHIOCARBAMATE

Intensität	Ag	Cu	Zn	Cr	Mn	Fe	U
ststst	8,14	4,05 3,61	7,03	7,77	6,34	8,48 7,62	7,51 4,39
stst		8,20 5,88	9,07 8,27 5,88	4,38	4,13	6,67 6,08 3,96	
stst	9,07	9,09 3,02 2,59	4,34 4,14 3,73	3,48	5,10 2,47	4,22	
m	4,32 3,27 2,26	7,20 6,82 4,42 4,23 2,76 2,26	3,58 3,08 2,78 2,05	4,98	3,56 3,16 2,75	2,75	5,77 5,20 2,82 2,52
s	4,88 3,37 3,12 3,01 2,89 2,42 2,01	4,69 2,03 1,99 1,77 1,75	4,94 4,71 4,51 2,86 2,64 2,33 2,27 1,74	6,91	4,51 3,44	5,00 3,27 3,12	3,40 3,90 2,64 2,25
ss		2,31 2,21 2,16 1,92 1,88 1,83 1,66 1,59 1,53 1,47				2,16 1,89	
sss	3,76 2,79 2,71 2,48 1,97 1,83 1,80 0,76 1,71	3,75 2,69 2,10 1,80 1,70	2,94 2,13 1,86 1,69 1,51	4,63 4,05 3,76	5,50 1,98 2,01 1,71 1,58 1,54 1,43	5,40 4,50 3,68 2,99 2,55 1,91 1,67 1,59	6,26 2,43 2,33 2,18 2,04 1,92

ststst = sehr sehr stark
 stst = sehr stark
 st = stark
 m = mittel

s = schwach
 ss = sehr schwach
 sss = sehr sehr schwach

TAFEL III. NETZEBENENABSTÄNDE EINIGER METALLPYRROLIDINDITHIOCARBAMATE

Intensität	Cu	Zn	Cd	Ni	Bi	Mn	Fe	Mo	Nb
ststst	3,58	7,56 4,18	9,32	7,13	9,44	4,53	4,68		7,30
stst	7,23 5,20 3,76			7,79 5,30 4,06	4,77 3,77		7,08	3,83	6,73
st	7,86 5,70	5,71 5,20 3,69 3,75	7,60 4,61 3,20	3,66	7,83 5,20	4,17	7,89 5,00 3,52	7,23	4,16
m	3,96 2,21 1,99	4,57 3,20	6,04 4,04 2,77 2,36	3,51	2,88 2,61	2,78	6,11 4,30 4,00 3,24 3,10 2,66 2,39	6,75 3,44	5,30 3,41
s	2,82 2,74 2,44 2,29	2,64 2,48 2,34 2,12' 1,98	3,78 3,29 2,15 1,98	5,60 4,28 3,28	7,20 5,82 3,09 2,73' 2,39 2,33		3,84 3,69 2,58 2,47 1,98 1,92	5,60	4,89 2,16
ss	4,54 2,50 2,04 1,94 1,86 1,82 1,76 1,62 1,58	3,55 3,02 2,89 2,75 2,25 2,19 1,81 1,75	2,26 2,02 1,90	3,78 2,72 2,58 2,35 2,19 1,81	3,29 2,49 2,27 1,97 1,78 1,63	3,42	5,40 2,78 2,29 2,10 2,06 1,81 1,75 1,69	5,30 4,53	3,74 2,08 2,00 1,92
sss	4,14 3,05 2,90 2,35 2,08 1,79 1,73 1,69 1,66	6,42 4,89 3,35 1,92	5,00 2,47 2,06 1,61	6,25 4,51 3,45 3,03 1,97	3,46 2,11 1,91 1,55	3,87	2,92 2,19 2,14	4,04 3,24	2,73 2,38 2,30

ststst = sehr sehr stark

stst = sehr stark

st = stark



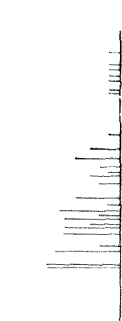





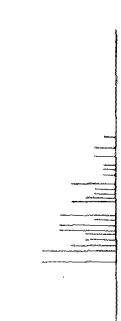


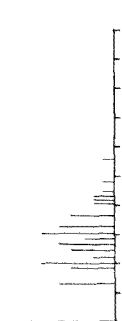
m = mittel

s = schwach


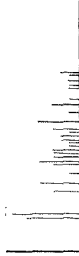

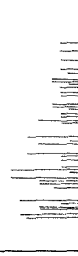

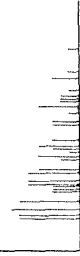



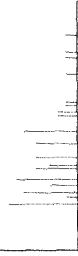

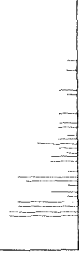

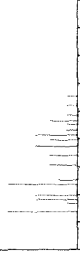
ss = sehr schwach

sss = sehr sehr schwach

TAFEL IV. DISUBSTITUIERTE CARBAMATE

Carbamat	Kristallhabitus	Debye-Scherrer-Diagramme	
<p>Natriumdiäthyl- dithiocarbamat</p> $\begin{array}{c} \text{S} \\ \\ \text{C}_2\text{H}_5 - \text{N} - \text{C} - \text{SNa} \\ \\ \text{C}_2\text{H}_5 \end{array}$	 <p>doppelbrechende, rhomboedr. farblose Kristalle</p>		
<p>Ammoniumdiäthyl- dithiocarbamat</p> $\begin{array}{c} \text{S} \\ \\ \text{C}_2\text{H}_5 - \text{N} - \text{C} - \text{SNH}_4 \\ \\ \text{C}_2\text{H}_5 \end{array}$	 <p>doppelbrechende, prismat. farblose Kristalle</p>		
<p>Natriumpyrrolidin- dithiocarbamat</p> $\begin{array}{c} \text{S} \\ \\ \text{H}_2\text{C}-\text{CH}_2 - \text{N} - \text{C} - \text{SNa} \\ \quad \quad \quad \\ \text{H}_5\text{C}-\text{CH}_2 \quad \quad \quad \text{H}_5\text{C}-\text{CH}_2 \end{array}$	 <p>doppelbrechende, prismat. farblose Kristalle</p>		
<p>Ammoniumpyrrolidin- dithiocarbamat</p> $\begin{array}{c} \text{S} \\ \\ \text{H}_2\text{C}-\text{CH}_2 - \text{N} - \text{C} - \text{SNH}_4 \\ \quad \quad \quad \\ \text{H}_5\text{C}-\text{CH}_2 \quad \quad \quad \text{H}_5\text{C}-\text{CH}_2 \end{array}$	 <p>doppelbrechende, prismat. farblose Kristalle</p>		


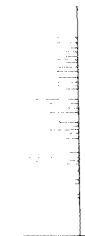













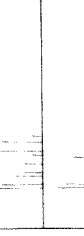

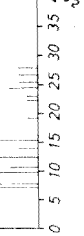
TAFEL V. METALL-DIÄTHYLDITHIOCARBAMATE

Metall	Formel Verhältnis Me: Carbamat	Kristallhabitus der aus Chloroform umkristallisierten Verbindungen †	Debye-Scherrer-Diagramme	d_{hkl} \AA
Ag	$\text{Ag}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]$ 1:1		farblos, würfelförmig	
Cu	$\text{Cu}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2$ 1:2		braun, langgestreckt, prismat.	
Zn	$\text{Zn}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2$ 1:2		farblos, schw. gelb, prismat.	
Cr ⁺³	$\text{Cr}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_3$ 1:3		blau- violett, prismat.	
Mn	$\text{Mn}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_3$ 1:3		rotviolett prismat. pyramidenförmig	
Fe	$\text{Fe}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_3$ 1:3		braun-schwarz langgestr. prismat.	
U	$\text{U}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_6$ * 1:6		rotgelb, würfel- förmig	

† Symbol — ist gleich 10μ für alle Metalle ausser für Zn, für das ist es 100μ .

* Bruttoformel ist noch nicht sicher, der Kohlenstoffgehalt spricht aber für die angegebene Verbindung.

TAFEL VI. METALL-PYRROLIDINDITHIOCARBAMATE

Metall	Formel Verhältnis Me:Carbamat	Kristallhabitus der aus Chloroform umkristallisierten Verbindungen†	Debye-Scherrer-Diagramme
Cu	$\text{Cu}(\text{C}_5\text{H}_8\text{NS}_2)_2$ 1:2		
Zn	$\text{Zn}(\text{C}_5\text{H}_8\text{NS}_2)_2$ 1:2		
Cd	$\text{Cd}(\text{C}_5\text{H}_8\text{NS}_2)_2$ 1:2		
Ni	$\text{Ni}(\text{C}_5\text{H}_8\text{NS}_2)_2$ 1:2		
Bi	$\text{Bi}(\text{C}_5\text{H}_8\text{NS}_2)_3$ 1:3		
Mn	$\text{Mn}(\text{C}_5\text{H}_8\text{NS}_2)_3$		
Fe	$\text{Fe}(\text{C}_5\text{H}_8\text{NS}_2)_3$ 1:3		
Mo	$\text{Mo}(\text{C}_5\text{H}_8\text{NS}_2)_3$ 1:3		
Nb	$\text{Nb}(\text{C}_5\text{H}_8\text{NS}_2)_3$ 1:3		

† Symbol — ist gleich 10μ .

gefundenen überein. G. Peyronel⁶ hat eine eingehende Studie über die Struktur des Ni-N-N-di-n-propyl-dithiocarbamates durchgeführt und für die Elementarzelle folgende Abmessungen gefunden: $a = 25,20 \text{ \AA}$, $c = 8,30 \text{ \AA}$ $c/a = 0,33 \text{ \AA}$ und das Volumen zu $4,564 \text{ \AA}^3$. Auf eine Elementarzelle kommen 9 Moleküle. Die Elementarzelle gehört dem rhombischen System an.

Den *Tafeln IV, V und VI*, die neben den Bruttoformeln, dem Kristallhabitus auch die Debye-Scherrer-Diagramme zeigen, kann im Augenblick nichts hinzugefügt werden, genügen aber zur röntgenographischen Identifizierung, wenn unter gleichen Bedingungen gearbeitet wird. Genauere Strukturbestimmungen sind Gegenstand weiterer Untersuchungen, worüber später berichtet werden soll.

Summary—The empirical formulae, crystal habits and X-ray patterns for a number of metal-carbamate complexes are presented.

Résumé—Les auteurs décrivent l'aspect extérieur cristallin et donnent les formules empiriques et les diagrammes de rayons X d'un certain nombre de complexes métal-carbamate.

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A NEW SENSITIVE AND SPECIFIC TEST FOR VANADIUM^V WITH SULPHOSALICYLIC ACID

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Summary—A very sensitive and specific test for vanadium^V is described using sulphosalicylic acid as reagent. When this reagent is brought into contact with solid vanadium^V (a drop of the test solution evaporated to dryness on a watch glass) in the presence of concentrated sulphuric acid or 80% syrupy phosphoric acid, a blue colour is developed. Using this colour reaction, it is possible to detect 0.05 μ g of vanadium^V in 0.05 ml of test solution. Aluminium^{III}, arsenic^V, beryllium^{II}, cadmium^{II}, chromium^{III}, chromium^{VI}, copper^{II}, iron^{III}, molybdenum^{VI}, nickel^{II}, tungsten^{VI}, uranium^{VI} and vanadium^{IV} do not interfere with this colour test, although some of them are known to form coloured complexes with sulphosalicylic acid under different conditions. Reducing agents like iron^{II}, uranium^{IV}, molybdenum^V and hydroquinone discharge the colour. The colour of the vanadium^V-sulphosalicylic acid compound is also discharged if the temperature is raised to 60°, though it reappears on cooling.

PANDU Ranga Rao and Gopala Rao¹ recently reported that quinquevalent vanadium develops at once a turquoise-blue colour when treated with salicylic acid in 20*N* sulphuric acid or syrupy phosphoric acid. This colour reaction, which was found to be almost specific, was utilised for the detection of very small amounts of vanadium^V. Cozzi and Raspi² found a somewhat similar colour reaction took place on treating vanadium with methyl salicylate in a medium containing hydrochloric acid, glacial acetic acid and acetic anhydride.

In this paper, a sensitive and a highly specific colour reaction is described for vanadium^V with sulphosalicylic acid in concentrated sulphuric acid or syrupy phosphoric acid. The colour developed by sulphosalicylic acid is both more sensitive and more stable than that with salicylic acid.

EXPERIMENTAL

Reagents

Sulphosalicylic acid, concentrated sulphuric acid or 80% syrupy phosphoric acid.

Procedure for the colour reaction in a test tube

One drop (0.05 ml) of vanadium^V solution and 1 drop of a 2% aqueous solution of sulphosalicylic acid are taken in a test tube, then concentrated sulphuric acid is added to make the total volume up to 2 ml. On mixing the contents, a greenish-blue colour develops immediately. The limit of identification was found to be 5 μ g of vanadium^V in a total volume of 2 ml.

Effect of temperature and light on the stability of the colour

At room temperature (28°) the colour slowly faded with time, taking several days for complete discharge. On raising the temperature, the colour began to fade at about 60° and became pale green at 80°. The intensity was regained to some extent on cooling to room temperature. When heated to higher temperatures, the colour was completely lost and was not restored on cooling. These observations indicate that the colour development is caused by the formation of a complex (between vanadium^V and sulphosalicylic acid) which dissociates at higher temperatures and reforms on cooling. On heating to above 80°, vanadium^V probably oxidises sulphosalicylic acid quite rapidly.

There was no significant change in the intensity of the colour at room temperature even after exposure to bright sunlight for 15 min.

Effect of acid concentration

The colour did not develop at all if the sulphuric acid concentration was below 4.5*M*. Above this acidity, the intensity of the colour increases with increase in acid concentration.

When the reaction was carried out using phosphoric acid instead of sulphuric acid, a clear blue colour was obtained, this colour being more stable than the greenish-blue colour developed with sulphuric acid. Further, it was observed that the colour began to develop even from 4*M* acidity in a phosphoric acid medium, the intensity of the colour increasing with increase in acid concentration. In a hydrochloric, nitric, perchloric or glacial acetic acid medium, the colour did not develop when aqueous solutions of vanadium^V and sulphosalicylic acid were used. However, it was possible to obtain a positive test for vanadium in these media if ammonium vanadate and sulphosalicylic acid were mixed in the solid state.

It is interesting to note that a bluish-black product is formed immediately on mixing solid ammonium vanadate with solid sulphosalicylic acid (but not with salicylic acid, acetylsalicylic acid, phenyl salicylate or methyl salicylate).

Interferences

Aluminium^{III}, arsenic^V, beryllium^{II}, cadmium^{II}, chromium^{III}, chromium^{VI}, copper^{II}, iron^{III}, molybdenum^{VI}, nickel^{II}, tungsten^{VI}, uranium^{VI} and vanadium^{IV} do not interfere with the test, although some of these ions are known to form coloured complexes with sulphosalicylic acid under different conditions. Cerium^{IV} and manganese^{VII} do not interfere with this colour reaction for vanadium^V provided a sufficient excess of the reagent is present. Substances like iron^{II}, uranium^{IV}, molybdenum^V, hydroquinone, etc, which reduce vanadium^V, should be absent.

Spot test procedure

If aqueous solutions of vanadium^V and sulphosalicylic acid are used for the test on a spot plate, the test is not very sensitive because of the two factors mentioned already, namely, the increase of temperature and lowering of acidity, both resulting from the dilution of the acid. However, the sensitivity can be very greatly increased by carrying out the test as follows:

One drop (0.05 ml) of the test solution is taken on a watch glass and evaporated to dryness on a water bath. After the watch glass has cooled to room temperature, 2 drops of concentrated sulphuric acid (or 80% syrupy phosphoric acid) are placed on the watch glass at a little distance from the residue and a small crystal of sulphosalicylic acid is intimately mixed in this acid. The mixture is allowed to flow on to the residue of vanadium^V by keeping the watch glass slightly inclined. At the boundary where the reagent mixture meets the residue of vanadium^V test solution, a fine blue line appears.

Limit of identification: 0.05 μg of vanadium^V per 0.05 ml of test solution.

Dilution limit: 1:1,000,000.

Acknowledgment—The authors wish to thank Prof. G. Gopala Rao for his interest in this work.

Zusammenfassung—Ein sehr empfindlicher Nachweis für Vanadin(V) wird beschrieben. Wenn Sulfo-salicylsäure mit festem Vanadin(V) Salz (ein Tropfen Probelösung auf einem Uhrglas zur Trockene eingedampft) in Kontakt gebracht wird, entwickelt sich in Gegenwart von conc. Schwefel- oder 80%iger Phosphorsäure eine blaue Färbung. Mittels der Reaktion ist es möglich 0.05 μg Vanadin(V) in 0.05 ml Lösung nachzuweisen. Al, As(V), Be, Cd, Cr(III), Cr(VI), Cu, Fe(III), Mo(VI), Ni, W(VI), U(VI) und V(IV) stören nicht, obwohl bekannt ist, dass manche der Ionen gefärbte Komplexe mit dem Reagens geben, wenngleich unter anderen Bedingungen. Reduzierende Reagenzien, wie Fe(II), U(IV), Mo(V) oder Hydrochinon bleichen die Farbe aus. Die Färbung verschwindet bei Erhitzen auf 60°C, erscheint jedoch beim Abkühlen wieder.

Résumé—Les auteurs décrivent une recherche du vanadium (V) très sensible et spécifique, utilisant l'acide sulfosalicylique comme réactif. Quand ce réactif est mis en contact avec du vanadium (V) solide (une goutte de la solution à essayer évaporée jusqu'à siccité sur un verre de montre), en présence

d'acide sulfurique concentré ou d'acide phosphorique sirupeux à 80%, il apparaît une couleur bleue. En utilisant cette réaction colorée, il a été possible de déceler 0,05 μg de vanadium (V) dans 0,05 ml. L'aluminium(III), l'arsenic(V), le béryllium(II) le cadmium(II), le chrome(III), le chrome(VI), le cuivre(II), le fer (III), le molybdène(VI), le nickel(II), le tungstène(VI), l'uranium(VI), le vanadium(IV) ne gênent pas cette réaction colorée, bien que certains d'entre eux soient connus pour former des complexes colorés avec l'acide sulfosalicylique dans différentes conditions. Les agents réducteurs comme le fer(II), l'uranium(IV), le molybdène(V), l'hydroquinone déchargent la couleur. La couleur du composé vanadium(V)-acide sulfosalicylique est aussi déchargée, si la température est élevée jusqu'à 60°, quoiqu'elle réapparaisse au refroidissement.

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TRIFLUOROMETHYL SULPHONIC ACID AS A TITRANT IN GLACIAL ACETIC ACID SYSTEMS

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Summary—Trifluoromethyl sulphonic acid in glacial acetic acid has been compared with perchloric acid in glacial acetic acid as a titrant in a limited number of cases. It does not appear that the reagent is likely to compete seriously with perchloric acid in non-aqueous titrimetry. Although comparable to perchloric acid in acid strength in acetic acid as well as in instrument response, it is unlikely that the considerably higher cost can be justified on the grounds of freedom from precipitate formation alone and no other advantageous feature has been observed which could justify this.

SEVERAL aliphatic and aromatic sulphonic acids have recently been examined¹ as titrants for use in glacial acetic acid systems. None of these have proved to be as useful as perchloric acid as a titrant in this medium but it is quite practicable to use them as they possess, as a class, the advantage of ensuring freedom from precipitate or gel formation when certain compounds are titrated. Potassium hydrogen phthalate, for example, the common primary standard for use in glacial acetic acid systems, persistently forms a precipitate with perchloric acid during titration, and this can lead to difficulties in some instrumental methods of end-point detection.

Trifluoromethyl sulphonic acid has recently been prepared² and described as one of the strongest known sulphonic acids; and it may even be one of the strongest of all known acids. In view of the interest shown in comparatively weak sulphonic acids as titrants, a comparison of the analytical possibilities of trifluoromethyl sulphonic acid with the conventional perchloric acid in glacial acetic acid has been made, using a representative selection of basic substances and experimental techniques.

EXPERIMENTAL

Reagents and apparatus

Perchloric acid, 0.1N in glacial acetic acid: B.D.H. commercially available material was used, freshly standardised against potassium hydrogen phthalate.

Trifluoromethyl sulphonic acid, 0.1N in glacial acetic acid: Potassium trifluoromethyl sulphonate* (4.5 g) and concentrated sulphuric acid (6 ml) were heated together in a microdistillation apparatus under reduced pressure (2 mm Hg). Distillation was stopped when the oil bath temperature reached 120°. The distillate consisted of 2 ml of a clear, fuming liquid and a white solid (presumably trifluoromethyl sulphonic acid monohydrate,³ which can be distilled from sulphuric acid) adhering to the receiver. The trifluoromethyl sulphonic acid was decanted from the solid, weighed, and diluted with glacial acetic acid to the requisite volume. It was standardised against potassium hydrogen phthalate.

Indicators: 0.5% solutions in glacial acetic acid of Crystal Violet, Oracet Blue B and α -naphtholbenzoin were used. The end-point shade obtained with the different compounds titrated was matched against that obtained during standardisation with the same indicator.

Potentiometric titrations. A sleeve-type calomel electrode and a glass electrode were used in conjunction with a direct-reading pH meter (Electronic Industries Ltd. Model 23). End-points were determined graphically.

* Kindly supplied by The Minnesota Mining and Manufacturing Co. Ltd.

High-frequency titrations: The simple one-valve instrument⁴ operating at 15 Mc/s modified as previously described⁶ was used. Owing to the precipitation of potassium perchlorate during titrations with perchloric acid, diphenylguanidine was preferred as the primary standard for use with this method of end-point detection rather than potassium hydrogen phthalate, which was used for the visual and potentiometric standardisations.

RESULTS

A comparison of the potentiometric titration curves obtained with trifluoromethyl sulphonic acid and perchloric acid in glacial acetic acid with diphenylguanidine and potassium hydrogen phthalate as standards is given in Fig. 1. The shape of the high-

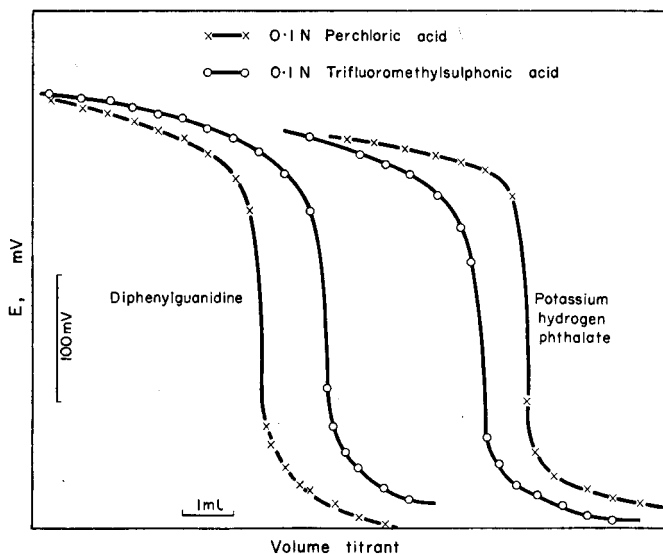


FIG. 1.

frequency titration curves obtained in the titration of diphenylguanidine and decamethylene-bis-pyridinium nitrate with both titrants is shown in Fig. 2. Results obtained with trifluoromethyl sulphonic acid for the determination of equivalent weights of a number of basic compounds of widely different constitution, on a semi-micro scale, are recorded in Table I.

Five separate determinations of the equivalent weight of a sample of commercial trinonylamine with both perchloric acid and trifluoromethyl sulphonic acid using Oracet Blue B as visual indicator gave the results shown in Table II.

DISCUSSION

The results show that perchloric and trifluoromethyl sulphonic acids are comparable titrants in glacial acetic acid systems. In potentiometric titrations trifluoromethyl sulphonic acid behaves as a very strong acid, and the height of the potential break and the maximum value of dE/dV (the rate of change of potential with volume of titrant) were almost identical with those obtained using perchloric acid. In this respect trifluoromethyl sulphonic acid is superior to the other sulphonic acids so far tested. As with other sulphonic acids, there was no trace of precipitation or gel formation when using potassium hydrogen phthalate as a primary standard, or indeed with any of the compounds so far examined.

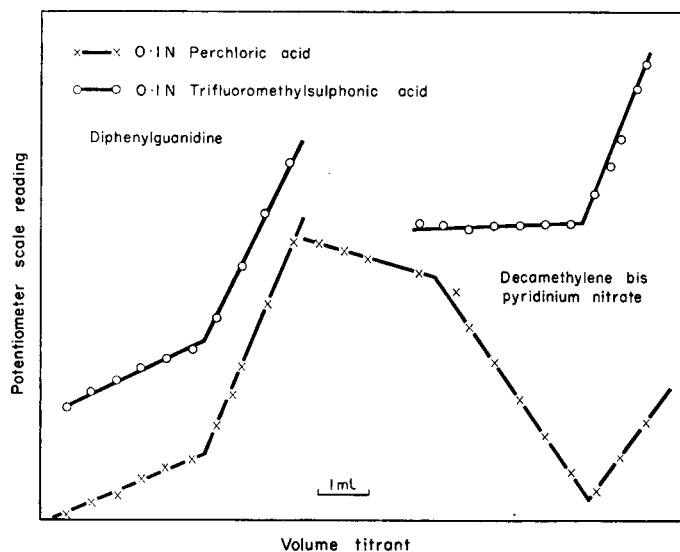


FIG. 2.

TABLE I

Compound	Method	Equivalent wt	
		Found	Required
Guanidine carbonate	Visual— α -naphthol-benzein	92	90
Ephedrine	Visual— α -naphthol-benzein	175	174
Diphenylguanidine	Visual—Oracet blue B	210	211
Diphenylguanidine	Potentiometric	211	211
Decamethylene-bis-pyridinium nitrate	High-frequency	210	211
Decamethylene-bis-pyridinium nitrate	Potentiometric	211	211
<i>o</i> -Phenanthroline hydrate	Visual—Oracet blue B	198	200
Tri-iso-octylamine	Visual—Oracet blue B	351	353

TABLE II

Titrant	Mean	Standard deviation	Required
Perchloric acid	399	3.6	395
Trifluoromethyl sulphonic acid	396	1.5	395

Using the high-frequency method of end-point indication, there was a slight advantage to be gained by the use of perchloric acid, as evidenced by the smaller angle between the intersecting lines obtained approaching and retiring from the end-point. Furthermore, whereas with perchloric acid information can often be gained from high-frequency titrations concerning the functionality of the compound being titrated, this effect was not noted when trifluoromethyl sulphonic acid was used. Decamethylene-bis-pyridinium nitrate, for example, gave two distinct end-points with

perchloric acid, corresponding to the titration of first one, and then both quaternary functions, but only one end-point, that corresponding to two quaternary groups, was detected during titration with trifluoromethyl sulphonic acid.

With visual indication of the end-points the precision obtained in the titration of trinyllamine with trifluoromethyl sulphonic acid was slightly better than when perchloric acid was used. The new titrant, however, was not as effective as perchloric acid for the titration of quaternary ammonium halides using the mercuric acetate method with Crystal Violet as indicator. When a representative selection of quaternary ammonium and phosphonium halides were titrated with trifluoromethyl sulphonic acid, only diffuse end-points were obtained. Several basic compounds were titrated visually with the new titrant, and satisfactory values of their equivalent weights were obtained.

Although new uses of trifluoromethyl sulphonic acid are being developed, it would appear doubtful from this limited assessment whether it will ever seriously compete with perchloric acid for use in non-aqueous titrimetry. Although comparable to perchloric acid in acid strength in acetic acid, as well as in instrument response, it is unlikely that the considerably higher cost can be justified on the grounds of freedom from precipitate formation alone, and no other advantageous feature has been observed which could justify this.

Zusammenfassung—Trifluoromethylsulfonsäure in Eisessig wurde mit Perchlorsäure in Eisessig als Titrationmittel verglichen. Es scheint nicht wahrscheinlich, dass das Reagens ernsthaft mit Perchlorsäure als Titrationmittel in nichtwässrigem Medium konkurrieren kann. Das Reagens ist zwar mit Perchlorsäure vergleichbar, soweit es die Stärke (in Essigsäure) und das Ansprechen des Instrumentes betrifft; es ist aber unwahrscheinlich, dass sich die beträchtlich höheren Kosten lediglich wegen Nichtauftretens von Niederschlägen rechtfertigen lassen. Dies ist der einzige auffindbare Vorteil.

Résumé—L'auteur a comparé l'acide trifluorométhylsulfonique dans l'acide acétique glacial à l'acide perchlorique dans le même solvant comme agent titrant dans un nombre limité de cas. Il ne semble pas probable que ce réactif concurrence sérieusement l'acide perchlorique dans la titrimétrie en milieu non aqueux. Bien que comparable à l'acide perchlorique au point de vue de sa force dans l'acide acétique, il est improbable que son coût très élevé puisse être justifié par la seule raison qu'il ne se forme pas de précipité et qu'aucun autre avantage n'ait été observé qui pourrait légitimer son utilisation.

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A STUDY OF THE CERIUM^{III}-ALIZARIN COMPLEXAN-FLUORIDE REACTION

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Summary—The optimum pH range of the cerium^{III}-alizarin complexanate method for fluoride has been established as pH 5.0–5.2 at which value the method may be applied over a wide concentration range from 5 μ g of fluoride ion (0.1 ppm) to 1.6 mg (>160 ppm) using a conventional spectrophotometer. The nature of the changes produced in the colour system by variation of pH are briefly discussed and the interference of 23 selected cations and 3 common anions has been examined. Practically all of the serious cationic interference can be overcome by the simple addition of a masking agent but, in a few cases, a preliminary extraction with 8-hydroxyquinoline and chloroform is required.

ALIZARIN complexan, 3[di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone, was first prepared for use as a complexometric indicator^{1,2} but it was later observed that the red chelates formed with cerium^{III}, lanthanum and praseodymium (and to a lesser extent with samarium) yielded blue water-soluble complexes with fluoride ion.³ The cerium^{III} chelate was selected for further qualitative and quantitative studies.^{4,5,6} The structure of the ternary complex has recently been defined and reasons for the unusual selectivity have been proposed.⁷

In the present investigation, the range has been extended from microgram to milligram amounts, and the effect of pH and time for the development of a stable colour have been studied more closely. The influence on the reaction of other ions which were not previously examined, or only examined superficially, has been established. Certain ions interfere seriously, but, in most instances, this effect can be overcome by the application of simple masking reactions.

Optimum pH range

In earlier work^{4,5,7} the reaction between fluoride and cerium^{III}-alizarin complexanate was carried out at pH 4.3, because at this pH the yellow to red acid-base transition of alizarin complexan just becomes apparent. Because the reaction was adjudged to be sufficiently sensitive (*ca* 0.1 ppm) and visually most easily observed at this pH, no further examination was then made of the permissible pH range. A study of this aspect is important, however, as will be seen subsequently.

In these experiments, sensitivity tests were carried out on fluoride ion at various pH levels using $5 \times 10^{-4}M$ solutions of alizarin complexan and cerium^{III} prepared by reduction of cerium^{IV} ammonium nitrate. A very slight excess of alizarin complexan was maintained over the normal 1:1 mole ratio with respect to cerium^{III}. These experiments extending from pH 3.5–12 indicated clearly (Fig. 1) that the optimum sensitivity of the fluoride reaction measured against the cerium^{III} chelate occurs at pH 5.0–5.2. In these particular experiments the solutions were only very lightly buffered with an acetic acid/acetate mixture (pH 4.3) and the pH was adjusted to the necessary value, using a pH meter, by careful addition of 1M sodium hydroxide or

1M hydrochloric acid. The effect of acetate ion recorded by other workers⁶ was observed, *viz.* stronger absorption at lower acetate ion concentration, but when later experiments were repeated using normal buffer formulations and normal 1:1 cerium to reagent ratio, optimum sensitivity was again found to lie in the pH range 5.0–5.2. Fig. 2 shows a cross section of the alteration in shape of the absorption curves produced by variation of pH in these initial experiments. Increase of hydroxyl ion concentration produces a hyperchromic effect on both the cerium^{III}-alizarin complexanate and the ternary fluoride complex. At pH 3.5 [Fig. 2(a)] both the cerium^{III} chelate and the

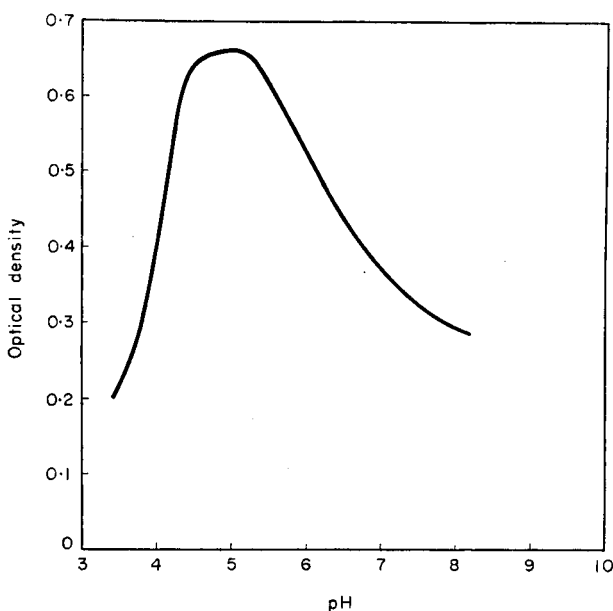


FIG. 1.—Influence of pH on sensitivity. 50 μg of F^- measured by procedure (A) in 4-cm cuvette against cerium^{III}-alizarin complexanate at 610 $m\mu$.

fluoride complex are largely dissociated as can be seen from the presence of the strong absorption band for free alizarin complexan at *ca.* 430 $m\mu$, but at $\text{pH} \geq 4.0$ [Fig. 2(B), (C), (D)] this band disappears. Fig. 3 shows the marked tendency for occurrence of a bathochromic shift of the wavelength of maximum band absorption for both the cerium^{III} chelate and the fluoride complex with increase of pH, over the range 3.5–6.2. Thereafter, the cerium^{III} chelate maintains a more or less unchanged wavelength of maximum absorption showing only a hyperchromic effect probably because of increased dissociation of the proton on the 1-hydroxyl group (*cf* Fig. 4).

On the other hand, from pH 6–12 there is observed for the fluoride complex a hyperchromic shift as above, and also a distinct hypsochromic change of wavelength of maximum absorption. This suggests that hydrolysis of the ternary fluoride complex (Fig. 4(d)) is occurring with replacement of the fluoride ion by hydroxyl.

In summary, these data indicate clearly that the method should not be operated beyond the range pH 4–6 and that the optimum sensitivity occurs at pH 5.0–5.2. At this dilution using $5 \times 10^{-4}M$ solutions of cerium^{III} and reagent, the time taken for stable colour development by the recommended procedure [*procedure(A)*] is 15 min

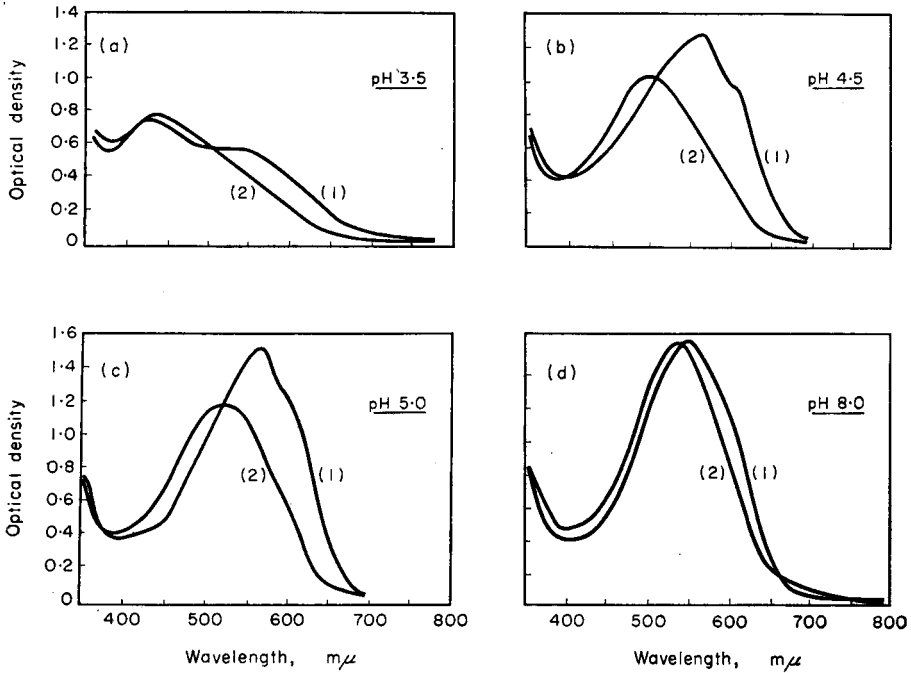


FIG. 2.—Effect of pH on absorption curves
 (1) Ternary fluoride complex.
 (2) Cerium^{III}-alizarin complexanate.
 (A) pH 3.5; (B) pH 4.5; (C) pH 5.0; (D) pH 8.0.

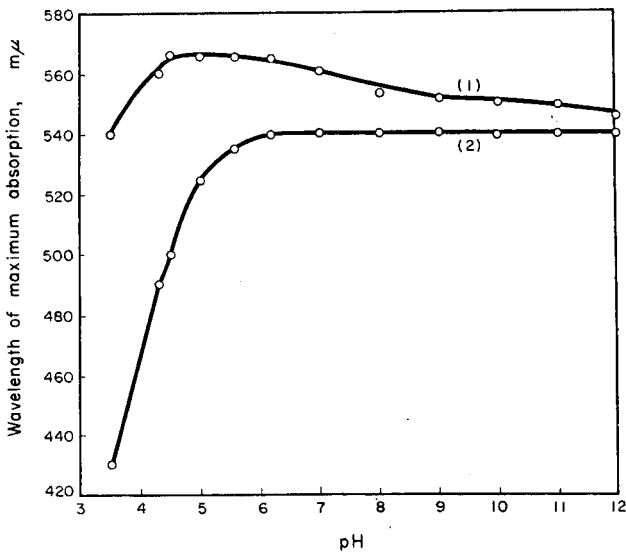


FIG. 3.—Influence of pH on maximum band absorption
 (1) Ternary fluoride complex.
 (2) Cerium^{III}-alizarin complexanate.

for the fluoride complex and 60 min for the cerium^{III} chelate against which it is measured. Once prepared, both colour systems remain unchanged for several days. Consequently it is recommended that a safe development time of 60–90 min should be allowed.

Concentration range

In earlier papers^{5,7} on the spectrophotometric determination of fluoride at pH 4.3, Beer's law was obeyed over the range 5–40 μg when the calibration curve was prepared from the recommended amounts of $5 \times 10^{-4}M$ solutions of cerium^{III} nitrate and

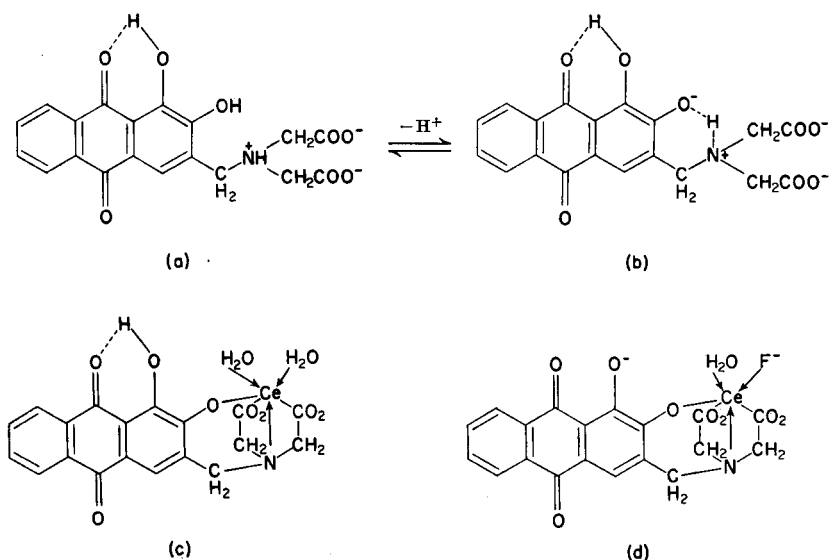


FIG. 4.—At pH 5.0–5.2 alizarin complexon exists as a mixture of the two ionisation stages (a) and (b); (c) cerium^{III}-alizarin complexonate; (d) ternary fluoride complex.

alizarin complexon. Subsequently, in applying the method to the semimicro scale, Johnson and Leonard⁶ did not attempt to use stronger reagent formulations but took an aliquot of the fluoride solution resulting from the decomposition of the compound, to obtain amounts of fluorine falling within the range of the submicro calibration curve, *i.e.* ca. 25 μg . This may involve dilution factors of more than 200 in some cases. Bartkiewicz and Robinson⁸ used the method over the range up to 10 ppm, but commented that at higher concentrations of fluoride ion the colour was bleached out. This observation indicates that insufficient attention was paid to the nature of the ternary fluoride complex and in all probability insufficient cerium^{III}-alizarin complexonate was added. The fact that large amounts of fluoride added to a fixed amount of the cerium^{III} chelate bleach the blue colour of the fluoride complex back to the free yellow alizarin complexon has already been stated by Leonard and West^{3,7} and is an obvious result of mass action and the insolubility of cerium^{III} fluoride. Because no serious attempt has been made to determine larger than microgram amounts of fluorine by this method, a series of experiments was initiated in which the concentration of all of the reagents involved was systematically increased in a step-wise fashion by factors of 10.

With $5 \times 10^{-3}M$ solutions of cerium^{III} nitrate and alizarin complexan, and a standard fluoride solution containing $50 \mu\text{g/ml}$, calibration curves were obtained up to $500 \mu\text{g}$. The calibration curve obeyed the Lambert-Beer law from 50 – $275 \mu\text{g}$; the straight line extension did not pass through the origin, but made a negative intercept on the optical density axis. This reaction [*Procedure (B)*] was carried out at pH 5.0 – 5.2 and measurements were made in 2 -mm cuvettes at $620 \text{ m}\mu$ which was the wavelength of maximum absorption of the fluoride complex measured against reagent.

When larger amounts of cerium^{III} and reagent were used, but still maintaining their $1:1$ mole ratio [*Procedure (C)*], a linear calibration curve was obtained over the range 100 – $550 \mu\text{g}$; up to $1000 \mu\text{g}$ the points still fall on a smooth curve falling only slightly below the linear projection of the lower part of the curve.

Finally, experiments were carried out with $10^{-2}M$ solutions of cerium^{III} and reagent at pH 5.2 . The wavelength of maximum absorption for the fluoride complex measured against the cerium^{III} chelate now shifted to $630 \text{ m}\mu$ and once prepared, remained unchanged for more than 4 days. The calibration curve followed the same pattern, being linear up to $800 \mu\text{g}$ and still lying on a smooth curve up to $1600 \mu\text{g}$. No attempt was made to extend the upper range of the method beyond this point.

It is appropriate here to mention that the pH and permissible concentration ranges are inter-related. Thus, whilst the method operates satisfactorily at pH 4.3 with $5 \times 10^{-4}M$ solutions, precipitation occurs at this pH with $5 \times 10^{-3}M$ solutions, particularly with the cerium^{III} chelate alone and with the lower amounts of fluoride ion. At pH 5.0 – 5.2 this difficulty is not encountered even with $10^{-2}M$ solutions. This effect of pH and the higher solubility of the fluoride complex compared to the cerium^{III} chelate agrees well with the proposed structure and protolysis mechanism suggested previously by Leonard and West.⁷ The minimum reaction time employed throughout these studies was 60 – 90 min though qualitatively the reaction appeared to proceed more rapidly in the more concentrated solutions.

Interferences

In the paper describing the spot-test procedure for fluoride⁴ it was found that the colour produced by $0.2 \mu\text{g}$ of fluoride was not interfered with visually by one hundred-fold mole ratios of sulphate, sulphide, chloride, bromide, iodide or cyanide. A six-fold excess of phosphate and the presence of moderately powerful complexing agents, such as iminodiacetic acid, partly suppressed the colour reaction whilst oxalate, citrate tartrate, uramildiacetic acid and EDTA interfered completely at $1:1$ ratios. In addition, it was found that aluminium, cobalt^{II}, copper^I, nickel, lead, iron^{III} and zinc prevented the formation of the blue colour. A ten molar amount of calcium caused slight inhibition whereas one hundred-fold excesses of mercury^{II}, manganese and magnesium showed no visible effect.

In quantitative experiments, a later study⁶ tested the interference of a few ions in the determination of $26 \mu\text{g}$ of fluoride ion at pH 4.6 . A 10% interference occurred with the following ions at the stated mole ratios: aluminium, 0.19 ; iron^{III}, 0.105 ; citrate, 0.36 ; phosphate, 7.7 .

In the experiments described below interferences were tested mainly at the $1:1$ mole ratio on a test solution containing $500 \mu\text{g}$ of fluoride ion. The results shown in Table I were obtained by the addition of the interfering ion to the fluoride solution and allowing the two to react for 30 min. Then in each case were added, successively, 25 ml

of $6.25 \times 10^{-3}M$ alizarin complexan solution, 5 ml of buffer solution (pH 5.2) and 25 ml of $5 \times 10^{-3}M$ cerium^{III} nitrate solution; the solution was allowed to stand overnight following dilution to 100 ml. At this point it should be noted that the interference can operate in any one (or combination) of three main ways: (1) formation of a stable complex with fluoride ion, thus preventing the formation of the blue colour; (2) formation of a more stable chelate than cerium^{III} with alizarin complexan, thus decreasing or increasing the absorption at 620 m μ according to its molecular extinction coefficient and wavelength of maximum absorption; (3) by formation of a stable complex with cerium^{III}, almost invariably decreasing the absorption at 610 m μ . For example a small amount of aluminium may cause a decrease by virtue of process (1) whilst a large amount may give high values by (2). The possibility also exists for a compensation of errors to result in no apparent interference though such a process would be unusual. Since most metal ions react to form complexes containing more than one fluoride ion and an excess of the interfering ion relative to fluoride requirements would therefore be present in all cases, an excess of *free* alizarin complexan was formulated in these particular experiments. This minimises the possibility of compensation by enhancing the absorbance of the foreign metal chelate without diminishing that of the cerium^{III} chelate unduly.

TABLE I. INTERFERENCE OF VARIOUS IONS WITH FLUORIDE METHOD.
THE RATIO $[M^{n+}]/[F^-] = 1$, EXCEPT WHERE STATED OTHERWISE. (500 $\mu g F^-$)

Ion	Amount taken, μg [Atomic ratio]	Interference, %	Ion	Amount taken, μg [Atomic ratio]	Interference, %
Ag	2806	2.5	Mg	632	1.4
Al	701	8	Mn ^{II}	1429	13.7
As ^V	1948	0.5	Ni	1526	145
Be	234	-54	Pb	5388	67.9
Ba	3573	2.5	Sr	2278	1.5
Ca	1045	-10.2	Tl ^I	5314	1.0
Cd	2922	92.5	V ^V	1324	10.0
Co	1532	135	Zn	1700	83.5
Cr ^{III}	2700 [2]	51.4	Zr	2372	1.6
Cu ^{II}	1653	64	B (as borate)	1125 [4]	-10
Fe ^{II}	1452	116	PO ₄ ³⁻	2471	-8
Fe ^{III}	1452	109	SO ₄ ²⁻	24,970 [10]	0.5
Hg ^I	5216	18.9			
Hg ^{II}	5216	7.0			

Large positive interferences occur with cadmium, cobalt^{II}, chromium^{III}, copper^{II}, iron^{II}, iron^{III}, nickel, lead, zinc and moderate interferences from aluminium, mercury^I, mercury^{II}, manganese^{II} and vanadium^{IV}. Large negative interferences occur with beryllium and moderate interferences from calcium, borate and phosphate. The interference of silver, arsenic^V, barium, magnesium, strontium, thallium^I, zirconium and sulphate does not appear to be serious. The moderate nature of the interference of aluminium and zirconium is surprising in view of the well known stability of their fluoride complexes; partial compensation may well account for the observed results because both also form stable chelates with alizarin complexan.

Elimination of interferences

In studying the elimination of interferences the normal 1:1 ratio of cerium^{III} to alizarin complexan was maintained and the normal procedure for 500 μg of fluoride [Procedure (C)] was followed with the amounts of interference specified in Table I.

An attempt was made first of all to add just sufficient EDTA to the test solution containing fluoride to complex the interfering metal ions. The necessary amount was found by complexometric titration on a separate aliquot of solution. In no experiment was this measure successful; low results were invariably found because of the partial complexing of the cerium^{III} by EDTA, in spite of the presence of the other free metals which had previously reacted with it.

Potassium cyanide masking was successful as specified for the complete elimination of the interference from copper^{II}, cobalt^{II}, mercury^I and mercury^{II}, and was only slightly unsatisfactory for manganese^{II}. The interference from cadmium and zinc was not entirely removed.

2,3-Dimercaptopropanol (BAL) completely eliminated the interference of nickel and lead. Similarly, an excess of sodium sulphide removed the interference of cadmium, zinc, and lead.

Aluminium was not masked by sodium diethyldithiocarbamate, tartrate or triethanolamine; iron^{III} was not masked by tartrate or by *o*-phenanthroline in the absence or presence of ascorbic acid; beryllium was not masked by phosphate or (added) acetylacetone; chromium^{III} was not masked by tartrate, calcium by *o*-phenanthroline or vanadium^V by reduction with ascorbic acid.

Because most of the metals which still interfere are known to react well with general-purpose reagents, such as cupferron and 8-hydroxyquinoline, attempts were made to add these as masking agents, but both caused interference with the control, particularly cupferron. Further experiments using 8-hydroxyquinoline revealed that this interference was caused by attack from the *excess* of reagent on the cerium^{III} and another series of tests was effected in which the excess of 8-hydroxyquinoline and the interfering metal-chelate were extracted at pH 5.0–5.2 *before* the addition of alizarin complexan and cerium^{III} nitrate. The interferences of aluminium, iron^{III}, chromium^{III}, and vanadium^V were completely removed by this simple expedient. Zirconium proved troublesome because of extremely stable emulsion formation, but it is known to be extracted⁹ under the conditions and consequently no further attempt was made to eliminate the emulsion formation since this is probably only a point of detail.

Calcium and beryllium are the only two remaining cationic interferences amongst the metals tested. They were not accounted for in this study, but it is logical to assume that their interference could readily be eliminated by a closely similar process. Calcium may be extracted as its 8-hydroxyquinolate by chloroform at higher pH values⁹ and beryllium by the closely related agent 8-hydroxyquinoline also in chloroform at pH 7.5–8.5.¹⁰ It is not known how well the beryllium would extract from a fluoride-containing solution, but in view of the performance of aluminium and iron^{III}, the procedure would be expected to be entirely successful for calcium if not also for beryllium. Another possibility which exists for beryllium is the extraction of its acetylacetone chelate at low pH.¹¹ Removal of the excess acetylacetone by extraction would doubtless remove the interference noted during the direct addition experiments described earlier in this paper (*cf.* also the direct addition of 8-hydroxyquinoline).

The extraction method based on 8-hydroxyquinoline should eliminate the cationic interference of a much wider range of metals than those examined in this study. Lastly, the removal of anionic interference by borate or phosphate would most probably require an ion-exchange separation, though the masking of borate interference by mannitol may be possible.

CONCLUSION

It has been shown that the optimum sensitivity of the cerium^{III}-alizarin complexan method for fluoride is obtained at pH 5.0–5.2. The working range of the method by suitable modification lies between 5 μg (0.1 ppm) to more than 1.6 mg (>160 ppm) at this pH range. Whilst the method works satisfactorily at pH 4.3 for dilute solution work, precipitation of the cerium^{III} chelate occurs at that pH when using $\geq 5 \times 10^{-3}M$ reagents. The wavelength of maximum absorption for measurement of the ternary fluoride complex against the cerium^{III} chelate shifts from 610 $m\mu$ with $5 \times 10^{-4}M$ to 620 $m\mu$ for $5 \times 10^{-3}M$ to 630 $m\mu$ for $10^{-2}M$ solutions.

The interference of 23 selected cations has been studied. In most instances it has been shown that the addition of a suitable masking agent, such as cyanide, 2,3-dimercaptopropanol or sulphide prevents interference, whilst for ions which are more difficult to mask, such as aluminium, chromium^{III} and vanadium^V, a simple preliminary extraction with 8-hydroxyquinoline and chloroform removes all interference.

EXPERIMENTAL

Reagents

$5 \times 10^{-4}M$ Alizarin complexan solution: Suspend 192.5 mg of alizarin complexan (a suitable grade of reagent is obtainable from Hopkin and Williams Ltd.), in freshly distilled water and add the minimum amount of 2*N* sodium hydroxide solution to ensure complete solution of the solid. Add dilute hydrochloric acid carefully till the violet colour of the solution turns to red (pH 5–6) and dilute to 1 litre.

Stronger solutions, e.g. $5 \times 10^{-3}M$, are prepared with proportionate amounts of reagent. Magnetic stirring is advisable to ensure complete solution and the colour in the flask should remain (just) violet to ensure complete solution before cautious addition of the hydrochloric acid during which the solution should be well mixed or agitated.

$5 \times 10^{-4}M$ Cerium^{III} nitrate solution: Prepare a solution of AnalaR cerium^{IV} ammonium nitrate (ca. 55 g/litre) and titrate against standard iron^{II} ammonium sulphate using ferroin as indicator. Dilute this stock solution to be exactly 0.1*M*. Take a suitable aliquot of the stock dilution, reduce to cerium^{III} by the addition of an excess of freshly prepared ascorbic acid solution and dilute to the mark. $5 \times 10^{-3}M$ cerium^{III} nitrate solution is similarly prepared.

Buffer solution (pH 5.0–5.2): Dissolve 100 g of AnalaR sodium acetate trihydrate in distilled water and add 11 ml of glacial acetic acid (pH meter 5.2). Dilute to 1 litre.

Standard fluoride solution: Dissolve 221.1 mg of (BDH extra pure) sodium fluoride in distilled water and dilute to 1 litre. This solution contains 100 μg of F^- per ml. More dilute solutions, e.g. 5 and 50* $\mu\text{g}/\text{ml}$, may be prepared by dilution.

$2.6 \times 10^{-2}M$ Solutions of interfering ions: Iron^{III} ammonium sulphate, nickel sulphate, copper chloride, calcium chloride, etc.

$2 \times 10^{-1}M$ Potassium cyanide solution: 1.3 g of potassium cyanide in 100 ml of water.

$5 \times 10^{-2}M$ Sodium sulphide solution: 1.2 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ /100 ml of water.

10% 2,3-Dimercaptopropanol solution: 10% V/V in aqueous ethanol.

2.26% 8-Hydroxyquinoline solution: 2.26 g in 100 ml of ethanol.

Chloroform

* $2.632 \times 10^{-3}M$ sodium fluoride solution contains 50 $\mu\text{g}/\text{ml}$ of F^- .

Apparatus

Unicam SP 600 spectrophotometer: With 4-cm and 2-mm cuvettes. The instrument was operated from the mains electricity supply via a stabilised 12V transformer.

Procedures

Procedure (A): 5–50 μg of fluoride ion (610 $\text{m}\mu$).

Pipette 1–10-ml aliquots of a 5 $\mu\text{g}/\text{ml}$ fluoride solution into 100-ml standard flasks, add 10 ml of $5 \times 10^{-4}M$ alizarin complexan solution and 2 ml of buffer solution (pH 5.0–5.2) from pipettes to each flask, followed by 10 ml of $5 \times 10^{-4}M$ cerium^{III} solution with constant swirling of the contents of the flask during the addition of the latter. Dilute the contents of each flask to 100 ml and set aside for 10 min. Prepare, simultaneously with the other solutions, a control solution containing no fluoride.

Measure the optical density (0.02–0.52) of the fluoride solutions against the cerium^{III}-alizarin complexanate control at 610 $\text{m}\mu$ in 4-cm cuvettes. The curve is linear from 5–35 μg , but falls off only very slightly at 50 μg .

Procedure (B): 50–500 μg of fluoride ion (620 $\text{m}\mu$).

Pipette 1–10-ml aliquots of a 50 $\mu\text{g}/\text{ml}$ fluoride solution into 100-ml standard flasks, add 10 ml of $5 \times 10^{-3}M$ alizarin complexan solution and 4 ml of buffer solution (pH 5.0–5.2) from pipettes to each flask, followed by 10 ml of $5 \times 10^{-3}M$ cerium^{III} solution with constant swirling of the contents of the flask during the addition of the latter. Dilute the contents of each flask to 100 ml and set aside for 90 min. Prepare, simultaneously with the other solutions, a control containing no fluoride.

Measure the optical density (0.027–0.32) of the fluoride solutions against the cerium^{III}-alizarin complexanate control at 620 $\text{m}\mu$ in 2-mm cuvettes. The curve is linear from 50–275 μg and falls off only slightly at 400 μg .

Procedure (C): 100–1000 μg of fluoride ion (620 $\text{m}\mu$).

Pipette 1–10-ml aliquots of a 100 $\mu\text{g}/\text{ml}$ fluoride solution into 100-ml standard flasks, add 25 ml of $5 \times 10^{-3}M$ alizarin complexan solution and 5 ml of buffer solution (pH 5.0–5.2) from pipettes to each flask, followed by 25 ml of $5 \times 10^{-3}M$ cerium^{III} solution, then proceed as in (B).

Measure the optical density (0.04–0.66) as above at 620 $\text{m}\mu$ in 2-mm cuvettes. The curve is linear from 100–550 μg and falls off only slightly at 800 μg .

Procedure (D): 200–1600 μg of fluoride ion (630 $\text{m}\mu$).

Pipette 2–16-ml aliquots of a 100 $\mu\text{g}/\text{ml}$ fluoride solution into 100-ml flasks, add 25 ml of $10^{-3}M$ alizarin complexan solution and 10 ml of buffer solution (pH 5.0–5.2) from pipettes to each flask, followed by 25 ml of $10^{-2}M$ cerium^{III} solution, then proceed as in (B).

Measure the optical density (0.134–1.085) as above at 630 $\text{m}\mu$ in 2-mm cuvettes. The curve is linear from 200–800 μg .

Elimination of interference

(a) *Masking procedures:* Pipette 10 ml of $2.6 \times 10^{-3}M$ sodium fluoride solution into a 100-ml flask followed by 1 ml of a $2.6 \times 10^{-2}M$ solution of the appropriate cation. Wash down the walls of the flask and allow to stand for 30 min. Add 1 ml of the appropriate masking agent and allow to stand for 5 min. Then apply *Procedure (C)* as usual.

(b) *Extraction procedure:* Pipette 10 ml of $2.6 \times 10^{-3}M$ sodium fluoride solution into a 100-ml flask followed by 1 ml of a $2.6 \times 10^{-2}M$ solution of the appropriate cation. Wash down the walls of the flask and allow to stand for 30–60 min. Add 5 ml of buffer solution (pH 5.0–5.2) followed by 1 ml 2:26% of 8-hydroxyquinoline solution. Some metals may be extracted almost immediately but with others, e.g. aluminium, it is best to allow precipitation to occur over the next 1.5–2 hr.

Extract the solution with three equal phase volumes of chloroform. Wash the combined chloroform extracts once with a half-phase volume of distilled water and add the washing to the original aqueous phase. Add 25 ml each of $5 \times 10^{-3}M$ alizarin complexan solution and, with constant swirling, $5 \times 10^{-3}M$ cerium^{III} nitrate solution. Dilute to 250 ml and develop the colour in the usual way for 90 min or overnight. Measure at 620 $\text{m}\mu$ in a 2-mm cuvette.

It is not necessary in the masking procedures to carry the reference cerium^{III}-alizarin complexanate solution through the same process, but it is advisable to do so in order to cater for impurities or small variations in experimental parameters such as pH. Standard fluoride solutions passed through the extraction process in the absence of foreign metal ions showed no significant increase or decrease in optical density.

Note: In all applications of the method it is important always to add the buffer solution and alizarin complexan solution before the cerium^{III} solution.

Zusammenfassung—Der optimale pH-Bereich der Cer(III)-Alizarinkomplexanmethode zur Bestimmung von Fluoride wurde zu 5–5.2 ermittelt. 5 µg (0.1 ppm) bis zu 1.6 mg (160 ppm) Fluorion können mit einem üblichen Spektrophotometer bestimmt werden. Einfluss des pH-Wertes auf die Färbung sowie die Störungen durch 23 Kationen und 3 Anionen werden diskutiert. Fast alle Kationenstörungen können durch Maskierung ausgeschaltet werden. Nur in airigen, wenigen Fällen ist vorherige Extraktion mit Oxin in Chlorform nötig.

Résumé—Le domaine de pH le plus convenable pour le dosage du fluorure par la méthode du complexe cérium(III)-alizarine est 5–5.2; à cette valeur de pH la méthode peut être appliquée dans un grand domaine de concentration: de 5 µg de fluorure (0,1 ppm) à 1,6 mg (160 ppm) en utilisant un spectrophotomètre ordinaire. La nature des changements produits dans le système coloré par variation du pH est brièvement discutée et l'interférence de 23 cations et de 3 anions ordinaires a été interprétée. Pratiquement l'interférence de tous les cations importants peut être surmontée par simple addition d'un agent complexant, mais dans certains cas une extraction préliminaire par la 8-hydroxyquinoléine et le chloroforme est nécessaire.

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A COMPARATIVE STUDY OF SOME LANTHANON CHELATES OF ALIZARIN COMPLEXAN AS REAGENTS FOR FLUORIDE

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Summary—A study has been made of the comparative suitability of the cerium^{III}, lanthanum and praseodymium chelates of alizarin complexan as reagents for the spectrophotometric determination of microgram amounts of fluoride. The cerium^{III} reagent is most sensitive at pH < 4.5 and the lanthanum reagent at pH ≥ 5.0. An enhancement of sensitivity may be obtained for both reagents at pH 4.3 by addition of acetone to 25% v/v, but the most sensitive means of determination is to use the lanthanum reagent in aqueous solution at pH 5.2 with measurement at 281 mμ. This procedure is 200% more sensitive than the standard method at 620 mμ.

LEONARD and West¹ have previously observed that fluoride ion forms soluble blue coloured ternary complexes with the red alizarin complexan chelates of the first few elements of the lanthanon series, *viz.* lanthanum, cerium^{III} and praseodymium. The fourth and fifth members of the series, neodymium and promethium, were not available but the ensuing rare earth, samarium, showed only slight colour formation and subsequent members showed no colour formation at all. At pH 4.3, the cerium^{III} reagent was found to be more sensitive than the others.

It has since been suggested² that the lanthanum reagent has advantages over the cerium^{III} reagent on the grounds of sensitivity, but comparative data have been

TABLE I. DIFFERENCE IN OPTICAL DENSITIES BETWEEN ALIZARIN COMPLEXAN CHELATES AND THEIR TERNARY FLUORIDE COMPLEXES

Wavelength of measurement, mμ	Difference in optical densities × 10 ³						
	pH 4.3				pH 5.7		
	Ce	La	Pr	Sm	Ce	La	Pr
590	186	171	147	19	174		35
600	194	172	152	13	174	182	40
610	199	173	161	6	200	207	50
620	188	165	152		204	210	52
630	160	135	128		178	184	42

lacking. In the present paper comparative studies have been made and a more sensitive procedure has been developed.

Reagents based on lanthanum, cerium^{III} and praseodymium were compared at pH 4.3 and 5.7 in sodium acetate buffers under carefully controlled conditions. The results shown in Table 1 were obtained with solutions containing 5×10^{-6} of a mole each of alizarin complexan, the lanthanon nitrate and sodium fluoride in a total volume of 100 ml. The lanthanon solutions were prepared from "Specpure" materials

and their stock solutions were standardised against EDTA using Xylenol Orange as indicator at pH 5.1, before dilution. These results indicate clearly that at pH 4.3, when interferences with the method are likely to be less than at higher pH values, the cerium^{III} reagent is slightly superior to those based on lanthanum and praseodymium. In all three cases the maximum sensitivity towards fluoride occurs at 610 m μ . The samarium-based reagent develops only a slight colour with fluoride and the maximum absorption occurs at 590 m μ . A gadolinium based reagent similarly formulated showed no optical activity whatsoever towards fluoride ion under these conditions. At pH 5.7 all three reagents showed maximum sensitivity towards fluoride ion at 620 m μ . It would appear that at this pH the ternary praseodymium complex is partly hydrolysed as there is a marked fall in absorption. There is a slight enhancement for cerium^{III}, but it is considerably more marked with the lanthanum reagent which at this pH is slightly (*ca.* 3%) more sensitive than the cerium^{III} reagent under the same conditions.

Comparison of lanthanum and cerium^{III} reagents over pH range 4.3–5.9

A narrower pH range was studied by preparing calibration curves (5–50 μ g) for fluoride ion based on 1:1 lanthanum and cerium^{III} chelates of alizarin complexan. Repeated check experiments revealed that at pH 4.3 (610 m μ) the cerium^{III} reagent was, as reported previously,¹ slightly more sensitive than the reagent based on lanthanum. At pH 4.5 (610 m μ) the difference in sensitivity between the two reagents becomes vanishingly small. At pH 5.1 (620 m μ) the lanthanum based reagent is approximately 4% more sensitive than the cerium^{III} reagent and this slight advantage is maintained at pH 5.5 and pH 5.9. At both of these pH values there is, however, a decrease in sensitivity for lanthanum as well as for cerium^{III}.

Enhancement of sensitivity

It has previously been reported that the ternary complex between cerium^{III}, alizarin complexan and fluoride ion may be extracted from aqueous solution with a non-miscible organic solvent.¹ In this process an enhancement of sensitivity is obtained. The enhancement, apart from the concentration factor, may be caused by the effect of lower dielectric constant favouring association of the complex and replacement of the co-ordinated water molecule still attached to the cerium^{III} ion in the ternary complex.¹ Accordingly, the effect of the addition of miscible solvents was examined because it was expected that a similar enhancement would result.

Four suitable solvents, two alcohols, one ketone and an ether were examined at pH 4.3, all at the same concentration (20% v/v). The results of this examination, shown in Table II, indicate the superiority (under the specified conditions) of acetone with its sterically unhindered keto-oxygen atom, relatively high basicity and low dielectric constant. Despite the basicity of its oxygen atoms, dioxan is nearly as effective as ethanol, presumably because of its lower dielectric constant. Similarly, methanol is less effective than the other solvents.

The cerium^{III} and lanthanum reagents were next compared in a 20% acetone medium and their performance was checked against variation of pH. This series of experiments revealed that acetone had a more pronounced effect on the lanthanum reagent. The optimum sensitivity in a 20% acetone medium was obtained at pH 4.3 and the wavelength of maximum difference shifted from 610 to 620 m μ . Under the

TABLE II. EFFECT OF SOLVENTS ON THE SENSITIVITY OF THE LANTHANUM METHOD
 5×10^{-6} MOLE OF LANTHANUM CHELATE + $25 \mu\text{g}$ OF $\text{F}^-/100 \text{ ml}$.

Wavelength of measurement, $m\mu$	Optical density $\times 10^3$											
	Methanol			Ethanol			Acetone			Dioxan		
	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity
	600	178	289	111	134	280	146	159	312	153	110	250
610	155	274	119	107	265	158	124	301	177	85	244	159
620	123	247	124	77	237	160	91	267	176	60	222	162
630	096	210	114	51	193	142	61	215	154	38	183	145

TABLE III. EFFECT OF ACETONE CONCENTRATION ON SENSITIVITY OF LANTHANUM REAGENT.
 5×10^{-6} MOLE OF LANTHANUM CHELATE + $25 \mu\text{g}$ OF F^- /100 ml

Acetone, %	Optical densities (at $620 \text{ m}\mu$) $\times 10^3$		
	Lanthanum chelate	Fluoride complex	Sensitivity
10	70	220	150
15	92	265	173
20	111	296	177
25	136	316	180
30	153	327	174
35	170	334	164

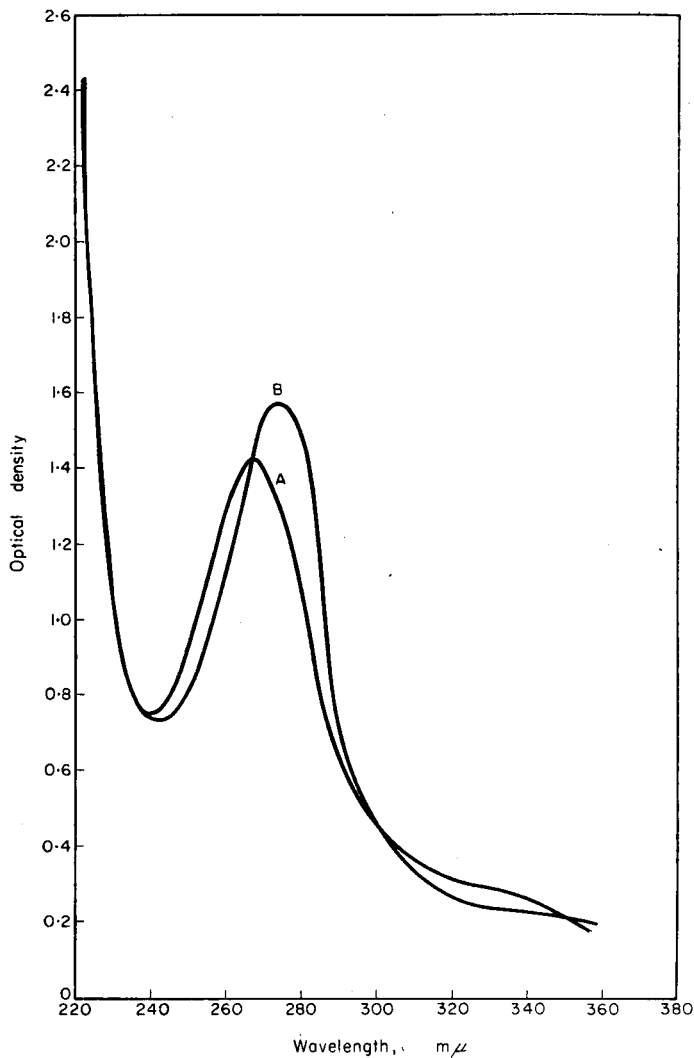


FIG. 1.—Absorption curves for cerium based reagent.
 A— 5×10^{-6} Mole of cerium chelate in 100 ml of solution, pH 5.2.
 B— 5×10^{-6} Mole of ternary fluoride complex in 100 ml of solution, pH 5.2.
 10-mm light path, measured against water.

optimum conditions the lanthanum reagent was *ca.* 3% more sensitive than the cerium reagent and 20% more sensitive than the lanthanum reaction in aqueous solution at the same pH. The "apparent" pH of these acetone solutions measured on a pH meter was 4.68.

Finally, in this series of experiments, the optimum concentration of acetone was

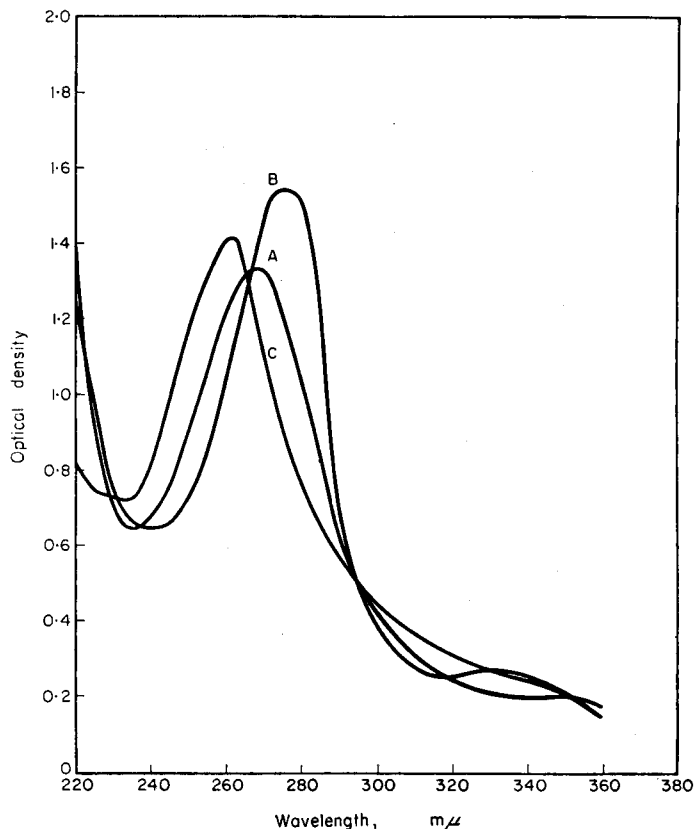


FIG. 2.—Absorption curves for lanthanum based reagent.

- A— 5×10^{-6} Mole of lanthanum chelate in 100 ml of solution, pH 5.2.
 B— 5×10^{-6} Mole of ternary fluoride complex in 100 ml of solution, pH 5.2.
 C— 5×10^{-6} Mole of alizarin complexan in 100 ml of solution, pH 5.2.

established for the lanthanum based reagent at pH 4.3. The results of this investigation are summarised in Table III and show clearly that the optimum concentration is 25%.

Absorption in the ultra-violet region

An examination of the mechanism of the fluoride reaction previously proposed by Leonard and West¹ and observation of absorption spectra of the chelate and ternary complex published in previous papers^{1,3} suggests that one would expect to get considerable absorption in the ultraviolet region. Accordingly, the ultraviolet spectra of the exactly formulated 1:1 chelates and 1:1:1 complexes for cerium^{III} (Fig. 1) and lanthanum (Fig. 2) were plotted. These reveal that there is a much stronger absorption

in the ultraviolet region and at the wavelength of maximum sensitivity (281 $m\mu$) the lanthanum method is slightly more sensitive (*ca.* 8%) than the cerium^{III} method. At the optimum pH of 5.0–5.2 the sensitivity of the lanthanum procedure is 200% greater at 281 $m\mu$ than at 620 $m\mu$.

Fig. 3 shows a series of calibration curves drawn up for the lanthanum reagent at

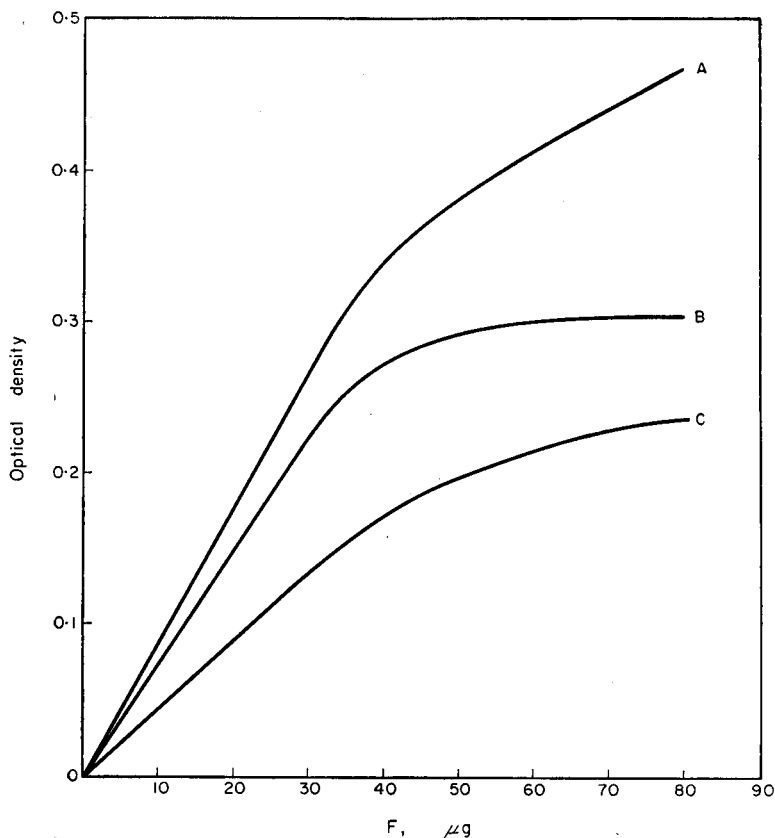


FIG. 3.—Calibration curves for lanthanum reagent.

- A— 5×10^{-6} mole of lanthanum chelate in 100 ml of solution, pH 5.2, 5–100 μg of fluoride, 10-mm silica cell at 281 $m\mu$.
 B— 5×10^{-6} mole lanthanum chelate in 100 ml of 25% acetone solution, pH 4.3, 5–100 μg of fluoride, 10-mm glass cell at 620 $m\mu$.
 C—As A, but using 10-mm glass cell at 620 $m\mu$.

pH 5.2 in aqueous solution at 620 and 281 $m\mu$ and at 620 $m\mu$ and pH 4.3 in a 25% acetone medium. This last curve flattens out much more markedly than those for the aqueous solutions beyond the upper level of the curve where the Lambert-Beer law is obeyed. It is noticeable also that the projection of these lanthanum curves passes through the origin.

CONCLUSION

The optimum sensitivity of the alizarin complexan method for fluoride is obtained with a lanthanum based reagent operated in aqueous solution at pH 5.0–5.2 with

measurements of optical density at 281 $m\mu$. Under these conditions the reaction is 200% more sensitive than that previously reported.³ Below pH 4.5 the cerium^{III} reagent is slightly more sensitive than the lanthanum reagent. Both are superior to a reagent based on the praseodymium chelate.

EXPERIMENTAL

Reagents

$5 \times 10^{-4}M$ Solutions of cerium^{III}, lanthanum and praseodymium nitrates: Prepared by dilution from accurately standardised (EDTA, pH 5.2, Xylenol Orange) 0.02M solutions made from "Specpure" materials (Johnson and Matthey).

$5 \times 10^{-4}M$ Alizarin complexan solution: cf. Reference 3.

Buffer solution (pH 5.0-5.2): 100 g of AnalaR sodium acetate trihydrate + 11 ml of glacial acetic acid dissolved in distilled water and diluted to 1 litre.

Standard fluoride solution: 5 μ g of F⁻/ml, cf. Reference 3.

Apparatus

Hilger "Uvispek" Spectrophotometer, 1-cm silica and glass cells.

Preparation of calibration curves

(A) Aqueous solution (620 $m\mu$) and (281 $m\mu$): Pipette 10 ml of $5 \times 10^{-4}M$ alizarin complexan solution into a 100-ml graduated flask, then add 2 ml of buffer solution (pH 5.0-5.2) and 1-10 ml of standard fluoride solution. Finally, add, with constant swirling of the contents of the flask, 10 ml of $5 \times 10^{-4}M$ lanthanum nitrate solution and dilute to the mark. Prepare similarly a control solution containing all of the reagents but no fluoride. Set the solutions aside for at least 1.5 hr and measure the optical density of the fluoride solutions in 10-mm cells [silica for 281 $m\mu$, 1 mm slit; glass for 620 $m\mu$, 0.05 mm slit] against the control solution.

(B) 25% Acetone solution: As above, but use 2 ml of buffer solution (pH 4.3) and add 25 ml of acetone after the addition of the lanthanum solution.

Analyses of unknowns

Take an aliquot of solution containing from 5-35 μ g (5-30 μ g for 25% acetone experiments) of fluoride in not more than 78 ml of solution and carry through the above procedure (A).

Note: For routine analytical work it is not necessary to use "Specpure" salts. Normal lanthanum nitrate hexahydrate may be used, but it must be standardised against EDTA, since the composition of the salt may be variable.

Acknowledgement—We are grateful to the Department of Scientific and Industrial Research for the provision of the Hilger and Watts "Uvispek" spectrophotometer used in this study.

Zusammenfassung—Die Eignung der Alizarinkomplexanchelate von Cer(III), Lanthan und Praseodym zur photometrischen Bestimmung von Mikrogrammengen Fluors wird verglichen. Das Cer(III) reagens zeigt höchste Empfindlichkeit bei pH-Werten unterhalb von 4.5 während das Lanthanreagens pH 5.0 oder höher verlangt. Ein Anstieg der Empfindlichkeit für beide Reagenzien wird beobachtet wenn bei pH 4.3 in 25 volumperzentiger Acetonlösung gearbeitet wird. Die höchste Empfindlichkeit wird mit dem Lanthanreagens erzielt bei pH 5.2 in wässriger Lösung unter Messen bei 281 $m\mu$. Diese Variante ist 200 mal empfindlicher als die Standardmethode bei 620 $m\mu$.

Résumé—Les auteurs ont étudié la valeur comparative des chélates du cérium(III), du lanthane et du praséodyme avec l'alizarine comme réactifs pour le dosage spectrophotométrique de quantités de fluorure de l'ordre du microgramme. Le réactif avec le cérium(III) est sensible à pH <4,5 et celui avec le lanthane à pH \geq 5,0. On peut augmenter la sensibilité des deux réactifs à pH 4,3 par addition d'acétone à 25%, mais la méthode de dosage la plus sensible est l'utilisation du réactif contenant le lanthane en solution aqueuse à pH 5,2 avec mesure à 281 $m\mu$. Cette méthode est deux fois plus sensible que la méthode standard à 620 $m\mu$.

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INFRARED CORRELATIONS IN THE BILE ACID SERIES

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Summary—The infrared spectra of a number of esters and free acids in the cholanic acid series have been examined with the aid of a special solvent system which overcomes the problem of solubility. Eleven absorption regions in the 9–12 μ region have been correlated with specific substitution on the steroid nucleus and side chain. In certain cases, perturbations were found when di- or tri-substitution occurred in rings A, B, and/or C.

INTRODUCTION

THE “finger-print” region of the infrared spectra of steroids (7–15 μ) has been of great use in characterisation of the stereochemistry of the A/B ring junction as well as of the substitution on the steroid nucleus. Estrogens,¹ progesterones,² cholesterol derivatives,³ as well as ketones,⁴ alcohols,⁵ and esters⁶ have been examined in this region with the purpose of correlating specific absorptions with particular functional groups in the molecule. Usually mono-functional compounds were examined because of the perturbations caused by different groups in polyfunctional compounds. Some studies indicated that satisfactory correlations may be obtained only when the substituted groups were widely separated in the molecule, as is found in 3,17- or 3,20-difunctional compounds.^{6,7}

The bile acid series of compounds has not been examined extensively. One deterrent has been the difficulty in dissolving these compounds in solvents suitable for infrared investigation. The polarity of the poly-hydroxylated acids, as well as their methyl esters makes it difficult using normal cell thickness to prepare solutions concentrated enough for examination of the inherently weak absorptions found in the “finger-print” region.

As noted by Ard and Fontaine,⁸ however, normally insoluble acids may be dissolved in infrared-suitable solvents if a small amount of basic compound, such as triethylamine, is also present. This innovation led to the formulation of a solvent system sufficiently transparent in the 6–6.5 μ and 9–12 μ regions. This system was used in the examination and correlation of certain specific group absorptions of mono-, di-, and tri-substituted bile acid compounds in these regions.

EXPERIMENTAL

The compounds examined and their sources are listed in Table I. The parent compound, cholanic acid, is shown in Fig. 1. Most substitution was at the 3, 7, and/or 12 positions. Chromatography, specific colour reactions, melting points, and lack of spectral change after recrystallisation were used as purification criteria. Purity was estimated to be at least 95% in all cases. Some compounds were demonstrated to be at least 99% pure by chromatographic techniques. Reagents used were reagent-grade except where noted otherwise.

* Deceased 3 June 1960.

TABLE I. COMPOUNDS EXAMINED AND THEIR SOURCES

1. Methyl cholanate	(a,b)*
2. Methyl lithocholate (3-hydroxy)	(a,c)
3. Methyl deoxy-cholate (3,12-dihydroxy)	(a,c)
4. Methyl chenodeoxy-cholate (3,7-dihydroxy)	(a,c)
5. Methyl hyodeoxy-cholate (3,6-dihydroxy)	(a,c)
6. Methyl cholate (3,7,12-trihydroxy)	(a,c)
7. Methyl 3-hydroxy-7-acetoxy-cholanate	(d)
8. Methyl 3-hydroxy-12-acetoxy-cholanate	(d)
9. Methyl 3-hydroxy-7,12-diacetoxy-cholanate	(d)
10. Methyl 3,7-diacetoxy-12-hydroxy-cholanate	(e)
11. Methyl 3-hydroxy-7-acetoxy-12-keto-cholanate	(e)
12. Methyl 3,12-dihydroxy-7-acetoxy-cholanate	(e)
13. Methyl 3,7,12-triacetoxy-cholanate	(f)
14. Methyl 3-keto-7-acetoxy-cholanate	(d)
15. Methyl 3-keto-12-acetoxy-cholanate	(d)
16. Methyl 3,7-diacetoxy-12-keto-cholanate	(e)
17. Methyl 3-keto-7,12-diacetoxy-cholanate	(d)
18. Methyl dehydrocholate (3,7,12-triketo)	(a,c)
19. Cholanolic acid	(b)
20. Lithocholic acid (3-hydroxy)	(c)
21. 7-Hydroxy-cholanolic acid	(g)
22. 12-Hydroxy-cholanolic acid	(d)
23. Deoxy-cholic acid (3,12-dihydroxy-)	(c)
24. Glycodeoxy-cholic acid	(h)
25. Chenodeoxy-cholic acid (3,7-dihydroxy-)	(e)
26. Glycochenodeoxycholic acid	(i)
27. 7,12-Dihydroxy-cholanolic acid	(d)
28. Hyodeoxy-cholic acid (3,6-dihydroxy)	(c)
29. Cholic acid (3,7,12-trihydroxy)	(c)
30. Glycocholic acid	(j)
31. 3-Hydroxy-7-keto-cholanolic acid	(k)
32. 3-Hydroxy-12-keto-cholanolic acid	(e)
33. 3,7-Dihydroxy-12-keto-cholanolic acid	(e)
34. 3-Acetoxy-cholanolic acid	(f)
35. 3,6-Diacetoxy-cholanolic acid	(f)
36. 3,7-Diacetoxy-cholanolic acid	(f)
37. 3,12-Diacetoxy-cholanolic acid	(f)
38. 3,7,12-Triacetoxy-cholanolic acid	(f)
39. 3-Keto-cholanolic acid	(a)
40. 3,7-Diketo-cholanolic acid	(a)
41. 3,12-Diketo-cholanolic acid	(a)
42. Dehydrocholic acid (3,7,12-triketo)	(c)
43. $\Delta^4,3$ -Keto bis nor cholenic acid	(c)
44. Stearic acid	(d)

*a. *Biochem. J.*, 1954, **55**, 292.

b. *J. Amer. Chem. Soc.*, 1949, **71**, 3301.

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i. *Arkiv. Kemi*, 1955, **8**, 331.

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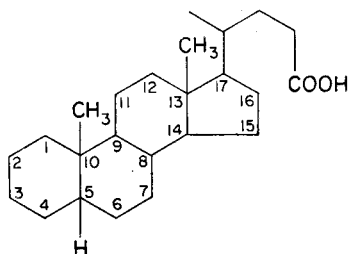


FIG. 1.—Structural formula of cholic acid.

By evaporation of an aliquot of an alcoholic standard solution at 110°, 0.01 to 0.02 millimoles of bile acid compound were placed in a 1- or 2-ml glass-stoppered volumetric flask. A fresh solution of 2% triethylamine (Matheson) in bromoform (Baker's "Purified") was prepared, and 0.3 ml was added to the cooled steroid residue in the flask, which was then stoppered and shaken to dissolve the compound. The infrared spectra were obtained on a Perkin-Elmer Infracord-137 instrument. The sample cell in all cases was 0.468 mm in thickness, and was scanned with a reference-cell (0.467 mm) containing the 2% triethylamine solvent. Calibration spectra were run periodically, and corrections were made on the steroid spectra when necessary. The wavelength accuracy was estimated to be within $\pm 0.02 \mu$ as determined by a calibrating polystyrene strip. Fresh solvent was prepared with each series of approximately 10 spectra, and the reference solution was changed for each compound. The results shown in Table II do not necessarily indicate all the absorption bands found in the 9–12 μ region; rather they indicate those absorptions where some degree of correlation is possible.

RESULTS AND DISCUSSION

Table II shows the wavelength and apparent molar absorptivities in the correlated regions. Absence of results indicates that the absorption in the specified region could not be differentiated from the background absorption at the concentrations used. Inflections have not been noted; obvious shoulders on the sides of strong absorption bands are, however, included. Usual background absorptivities were in the range of 10–30 units. Tentative assignments of various functional group absorptions are shown in Table III.

Because reaction of the acidic solute with the basic solvent usually increased the background absorption, a base-line technique was used to calculate absorbances and molar absorptivities. In all cases a straight line parallel to the 100% transmittance line was drawn through the absorption at 5.4 μ , which was the point of minimum absorption in most of the spectra. The absorbance of the compound was then calculated by subtracting the base-line absorbance from the absorbance indicated by the spectrum. The apparent molar absorptivities were calculated from the following formula:

$$a_M = A(MW)/c(d),$$

where A = absorbance, MW = molecular weight, c = concentration in mg/ml, and d = thickness in cm.

Anomalies in spectra of compounds in potassium bromide pellets have been noted by other investigators.^{9,10,11} This has been shown to be particularly true with compounds containing hydroxyl groups.¹² For this reason it was decided that for the most reproducible results, solution techniques were necessary.

Ard and Fontaine⁸ indicated that if 1–2.5% solutions of triethylamine in either carbon disulphide or carbon tetrachloride were used to dissolve acids for infrared sampling, the neutralisation of the acid by the base could cause some change in the

TABLE II. ABSORPTION BANDS

Compound	6.25 μ and 9-10 μ bands				10-11 μ bands*					
	6.25	9-32	9-65	9-71	9-78	9-89	10-22	10-32	10-56	10-65
1			9-65s† (48)	9-72 (144)		9-88 (60)			10-60 (19)	
2			9-65 (261)	9-70 (94)		9-88 (93)			10-58 (36)	
3				9-72 (294)		9-87 (107)			10-56 (63)	
4		9-33 (172)‡				9-85s (106)	10-22 (183)	10-32 (47)		
5		9-31 (177)				9-85s (160)¶	10-21 (138)		10-54 (71)	10-64 (61)
6		9-35 (132)		9-72s (138)	9-82 (181)	9-86s (280)¶		10-33 (124)		
7				9-70 (324)	9-70 (324)			10-32 (112)	10-53 (43)	10-66 (56)
8		9-35 (153)		9-72s (280)	9-80 (281)			10-32 (137)		10-64 (88)
9		9-40 (137)			9-77 (346)			10-33 (101)		10-66 (65)
10		9-35s (134)		9-73s (190)	9-80 (196)			10-31 (107)		10-63 (77)
11		9-35 (185)		9-73s (220)	9-80s (215)			10-30 (119)		10-65 (74)
12		9-35 (102)			9-78 (455)			10-35 (137)		10-65 (63)
13					9-82 (146)			10-31 (72)		
14					9-75 (175)			10-32 (103)		
15					9-78 (299)			10-32 (98)		10-65 (78)
16		9-41 (101)			9-78 (228)	9-91 (67)		10-32 (101)		10-65 (58)
17										
18	164‡									
19	169									
20	172			9-72 (208)		9-91 (106)	10-22 (75)		10-58 (81)	
21	172			9-70 (75)		9-91 (63)			10-60 (65)	
22	182					9-91 (63)			10-59 (51)	
23	175					9-88 (107)			10-6-7 (53)	
24	280s					9-88 (121)		10-33 (63)	10-59 (109)	
25	165			9-71 (112)		9-90 (76)	10-23 (180)	10-31 (53)	10-58 (88)	
26	232s	9-32 (153)		9-71 (111)		9-89 (65)	10-23 (165)			
27	181	9-32 (153)		9-72 (134)			10-20 (77)			
28	164			9-73 (285)				10-53 (60)		
29	174					9-86s (98)				
30	282s	9-32 (174)				9-87s (108)	10-22 (135)		10-53 (85)	
31	178	9-32 (181)		9-6-7 (98)		9-91 (103)	10-22 (119)		10-53 (62)	
32	170	9-33 (103)		9-71 (246)			10-25 (98)			
33	162			9-6-7 (123)			10-22 (80)			
34	172	9-32 (146)				9-86s (84)		10-33 (84)	10-54 (54)	
35	183									
36	165						10-22 (86)			10-64 (86)
37	168	9-41 (101)		9-76 (215)	9-76 (428)		10-22 (101)			
38	182			9-79 (288)	9-75 (358)			10-34 (122)		
39	195	9-35s (75)		9-78 (450)				10-30 (76)	10-59 (50)	
40	172			9-6-7 (65)		9-88s (41)		10-35 (86)		
41	184			9-6-7 (47)		9-91s (42)				
42	135			9-6-7 (75)		9-90s (62)				
43	185s			9-6-7 (73)		9-91 (70)				
44	157			9-6-7 (56)						
				9-6-7 (58)						

* See text for correlation of 11.6 and 12.0 μ bands.

† s-Shoulder.

‡ Apparent molar absorptivity.

¶ Approximate.

TABLE III. SUMMARY OF TENTATIVE SPECTRAL CORRELATIONS

Wavelength, μ	Functional group
6.25	Carboxylate ion (170)*
9.32	3,7-Bifunctional compounds (145)
	All acids (50)
9.65	12-Hydroxyl group (222)
	Ketones (70)
	All compounds (60)
9.71	3-Hydroxyl and 7-hydroxyl groups (see text)
	General (see text)
9.78	Mono-acetates (188)
	Di-acetates (314)
	Tri-acetates (453)
9.89	Most 3-hydroxy compounds without 7-hydroxyl group (106)
	General (85)
10.22	7-Hydroxyl group (134)
10.32	Acetates (107)
10.56	12-Hydroxy group (74)
	Many others
10.65	7-acetates (72)
11.65	Methyl esters (30)
12.0	Acids (80)

Average apparent molar absorptivity

spectra and give rise to some absorption bands not otherwise present. In order to study more fully the effect of solvent composition on solubility of the bile acid compounds, as well as the effects on the spectra obtained, a series of mixtures was prepared using varying percentages of triethylamine in different solvents. Compounds dissolved in 1% and 2% triethylamine solutions of the same solvent yielded essentially the same spectra although some of the compounds were less soluble in the 1% solution. When the concentration of triethylamine was increased to 3%, the absorption band of the amine at 9.1 μ became intense enough to render the region from 9.0–9.3 μ less useful. It was therefore decided to use a 2% solution of triethylamine in a suitable solvent for further investigations. In 0.3 ml of this solvent there is approximately 0.05 millimole of base, approximately three times the amount of steroid involved, so that an adequate excess is provided for complete neutralisation of free acids. Carbon tetrachloride and carbon disulphide, even with added triethylamine, were not capable of dissolving some of the hydroxylated compounds, even when warmed. The use of methylene chloride, bromodichloromethane, dibromochloromethane, and trichloroethylene was investigated, but it was found that either they had poor solvent power or they obscured large regions of the "finger-print" region. Chloroform possessed the solvent properties, but had intense absorptions in the 9–12 μ range. Bromoform, however, was quite transparent in this spectral range, and had good solvent properties for all the compounds investigated, and a 2% triethylamine solution was used for this study. The following is a discussion of each of the correlated regions—

6.25 μ : It has been noted that upon neutralisation of carboxylic acids, the absorption at 5.75 μ disappears to be replaced by two strong bands at longer wavelengths.¹³ The basicity of triethylamine in the solvent caused this neutralisation of free acids,

and the carboxylate ion bands appear at 6.25 and 7.2 μ . No absorption is found in the carbonyl region if compounds containing only carboxyl and hydroxyl groups are dissolved in this basic solvent. Obviously ketones and esters will yield intense carbonyl absorptions if present. This technique therefore is a rapid method for detecting the presence of carbonyl groups in carboxylic acids without resorting to the preparation of derivatives. As indicated in Table II, all the carboxylic acids yield relatively intense absorptions in the 6.25 μ region. Apart from the three glycine conjugates (24, 26, 30) and the Δ^4 , 3-keto compound (44), which, because of other strong bands in the region, do not yield a separate band for the carboxylate group, the average molar absorptivity, irrespective of other functional groups present, is 171 litre mole⁻¹ cm⁻¹ with an average deviation of 8 units.

9.32 μ : Absorption in this region is indicative of the simultaneous presence of carbon-oxygen bonds at carbons-3 and -7. As shown in Table II, compounds having hydroxyl groups at both positions (4,6,25,26,29,30,33) have strong absorption bands in the 9.31–9.33 μ range. Compounds which contain the 3-hydroxyl and 7-acetoxy groups simultaneously have the absorption shifted to 9.35 μ (7,9,11,12). Compounds having acetoxy groups at both the 3 and 7 positions (10,16,13,36) have the absorption shifted to still longer wavelengths, at 9.40–9.41 μ . The two tri-acetoxy compounds (13,38) also have absorptions shifted to longer wavelengths, although the band is found as a shoulder on the side of the very intense acetate absorption band at 9.8 μ . 3-Hydroxy-7-keto-cholanic acid (31), the only 3-hydroxy-7-keto compound studied, also has a reasonably strong absorption band at 9.33 μ . It is probable that as the hydroxyl groups are acetylated, the absorption band is shifted progressively to longer wavelengths, although the absorptivity remains about the same, the average for the seventeen compounds being 144 litre mole⁻¹ cm⁻¹. All free acids examined also have a small absorption band in this region. However, the absorptivity is always less than 50 units and is easily differentiated from the much more intense 3,7-bifunctional vibration.

9.65 μ : All compounds were found to have some absorption in the order of 50–70 units in this region, although it was rather diffuse, and precise wavelengths could not be assigned. All ketones were also found to have rather general absorption from 9.6–9.8 μ with absorptivities ranging from 50–100 units. The strong, sharp absorption of the 12-hydroxy compounds (3,10,6,12,22,23,24,27,29,30) from 9.64–9.68 μ , however, was readily apparent and easily differentiated from the more diffuse absorption. Apart from 12-hydroxy- and 7,12-dihydroxy-cholanic acids (22,27), the molar absorptivities of these compounds range between 190 and 314 units. Apparently the presence of substitution at carbon-3 enhances the 12-hydroxyl group vibration.

9.71 μ : As noted in the previous section, all compounds have weak absorption in this region, especially the ketones, the absorptivities generally being less than 70 units. It is apparent from Table II that all compounds with either a 3-hydroxyl or a 7-hydroxyl group also have intense absorption in this region. The three cholate compounds have this region obscured by the strong 12-hydroxyl vibration at 9.65 μ . The 7-hydroxyl group absorption itself is comparatively weak as indicated in 7-hydroxy- and 7,12-dihydroxy cholanic acids (21,27); even when a hydroxyl group is also present at carbon-3, the average molar absorptivity is about 110 units (4,25,26,33). On the other hand, the ten 3-hydroxy compounds with no hydroxyl group at carbon-7

have an average molar absorptivity of 223. This would seem to indicate that the simultaneous presence of the hydroxyl group at carbon-7 decreases the absorption from 3-hydroxyl groups. The infrared absorption of the 3-hydroxy compounds with no other substitution in rings A, B, or C has been studied and this structure was found to absorb at a slightly longer wavelength than found in this study.^{5,7} This is apparently caused by the differences in polarity of the solvents used.

9.78 μ : Acetate groups are characterised by having relatively intense absorption bands in this region. Molar absorptivities range from 146–455 for mono-, di-, and tri-acetates. 3-Acetates have also been examined by other investigators and found to have absorption in this region.^{6,14} The presence of keto groups seems to depress the absorption of the acetate group in most cases. The molar absorptivity of methyl-3,7-diacetoxy-12-keto-cholanate (16) is 14% less than that of methyl-3,7-diacetoxy-cholanate (10). It is 19% less in the case of methyl-3-keto-7-acetoxy-cholanate (14) and methyl-3-hydroxy-7-acetoxy-cholanate (7). There is also a 19% decrease in the case of methyl-3-keto-7,12-diacetoxy-cholanate (17) and methyl-3-hydroxy-7,12-diacetoxy-cholanate (9). The 86% increase in the absorptivity of methyl-3-hydroxy-12-acetoxy-cholanate (8) as compared with methyl-3-keto-12-acetoxy-cholanate (15) probably arises from the overlapping of the 3-hydroxyl absorption at 9.70 μ with the acetate absorption at 9.75 μ , which causes one strong band to occur at 9.70 μ . Except for this compound, mono-acetates have absorptivities of 146–215 with an average of 188 units. Diacetates have a range of 228–428 units with an average of 314, and the two tri-acetates have an average of 453 units. From these results it appears that the introduction of each acetoxy group, whether substituted at the 3, 7, or 12 position, increases the absorptivity approximately 130 units.

9.89 μ : Almost all compounds containing acetate groups have this region obscured by the intense absorption at 9.75 μ . Two acetates, however, methyl-3-hydroxy-12-acetoxy-, and 3-hydroxy-7,12-diacetoxy-cholanate (8,9), have shoulders on the side of the acetate band, but accurate determination of absorptivities was not possible. Of the remaining compounds, almost all show some absorption in this region, ketones and most of the 7-hydroxy compounds having absorptivities less than 85 units. Compounds containing a 3-hydroxyl group have increased absorption, with absorptivities ranging from 93–121 units, the average for nine compounds being 106.

10.22 μ : Absorption in this region is characteristic of all 7-hydroxy compounds. However, the six compounds which also contain a 3-hydroxyl group (4,6,25,26,29,30) have an average molar absorptivity twice that of 7-hydroxy- and 7,12-dihydroxy-cholanic acids (21,27). The marked enhancement apparently arises from the interaction of the 3- and 7-hydroxyl group vibrations. The only exception to this correlation is 3,7-dihydroxy-12-keto-cholanic acid (33), although it has an uncorrelated and unexplained band at 10.33 μ . Also having absorptions in this region are 3-hydroxy-7-keto- and 3-hydroxy-12-keto-cholanic acids (31,32), although no other 3-hydroxy compounds have similar absorptions except those also containing the 7-hydroxyl group. Two acetates, 3-acetoxy-, and 3,6-diacetoxy-cholanic acids (34,35), also have absorption in this region. These bands, however, are probably the acetate absorptions shifted down from 10.33 μ (see next section).

10.32 μ : Absorption in this region is characteristic of acetate groups on the steroid molecule. Fourteen acetoxy compounds have molar absorptivities ranging

from 76–137 units with an average of 107. The only acetoxy compounds examined which showed no absorption were 3-acetoxy- and 3,6-diacetoxy-cholanic acids (34,35). However, both of these compounds have unexplained absorption bands of similar intensities at $10\cdot22\ \mu$ which are probably due to shifting of the $10\cdot32\ \mu$ band. The three deoxy-cholic acid compounds (23,24,33) also have bands in this region, although the absorptivities are significantly lower. The only other compound absorbing in this region is 3,7-dihydroxy-12-keto-cholanic acid. This may be the 7-hydroxyl group band that should appear at approximately $10\cdot23\ \mu$ but is shifted because of the presence of the 12-keto group.

$10\cdot56\ \mu$: Correlation in this region is less definite than the preceding ones. All 12-hydroxy compounds (3,6,22,23,24,27,29,30) have intensities of 53–109 units except for two compounds (10,12) which have this region obscured by strong absorption at $10\cdot63\ \mu$. Many other compounds, however, have significant absorption in this region, as indicated in Table II, and still others show inflections on the sides of other strong bands. No final correlation could be made.

$10\cdot65\ \mu$: All 7-acetoxy compounds have absorption in this region, molar absorptivities ranging from 56–93 units, with an average of 72 for the ten compounds. No other compounds absorbed in this region.

Miscellaneous absorptions: All methyl esters examined have an absorption band at $11\cdot6$ – $11\cdot7\ \mu$ with absorptivities between 15 and 40 units. Also, all acids have absorption at $11\cdot98$ – $12\cdot03\ \mu$, the majority of the absorptivities falling between 75 and 85 units. Although these absorptions are relatively weak, they are readily

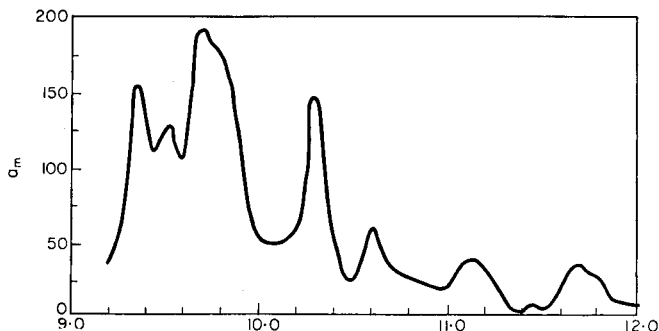


FIG. 2.—Summation spectrum.

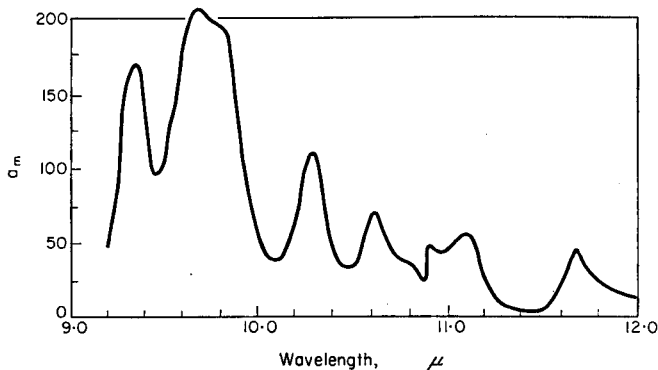


FIG. 3.—Spectrum of methyl-3-hydroxy-7-acetoxy-cholamate.

apparent in the spectra of the compounds. Differentiation between the spectra of free acids and their methyl esters is easily made by examination of these two regions. Except for these bands, the spectra of the free acids and their methyl esters in the 9–12 μ range were indistinguishable.

Summation spectra: Although some studies have indicated the possibility of preparing summation spectra of complex molecules by using the absorptivities of simpler molecules, the preparation has not been attempted with steroids with functional groups in close proximity.^{6,7} This attempt has been made in the present study. Fig. 2 illustrates the summation spectrum produced by adding the apparent molar absorptivities of methyl 3-hydroxy-7-acetoxy-cholanate (7) and 12-hydroxy-cholanic acid (22) and subtracting the values of cholanic acid (19). This should yield the spectrum of methyl-3,12-dihydroxy-7-acetoxy-cholanate (12), shown in Fig. 3. It is evident that these spectra are quite similar in spite of the presence of substitution in rings A, B, and C. This indicates the possibility of preparing summation spectra of more complex molecules. However, certain combinations of functional groups such as found in 3,7-dihydroxy compounds make this difficult because of perturbations.

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Zusammenfassung—Die Infrarotspektren einer Anzahl von Estern und freien Säuren der Cholan-säurereihe wurden untersucht, wobei ein besonderes Solventsystem verwendet wurde um die Lösungsschwierigkeiten zu beheben. Elf Absorptionsbereiche zwischen 9 und 12 μ wurden spezifischen Substituenten im Steroidkern und der Seitenkette zugeordnet. In bestimmten Fällen wurden Störungen beobachtet, wenn Di- oder Trisubstitution in den Ringen A, B und/oder C auftrat.

Résumé—Les spectres infra-rouge d'un certain nombre d'esters et d'acides libres dans la série de l'acide cholanique ont été examinés grâce à un solvant spécial qui résout le problème de la solubilité. Onze domaines d'absorption dans la région 9–12 μ ont été reliés à la substitution spécifique sur le noyau stéroïde et la chaîne latérale. Dans certains cas, les auteurs ont trouvé des perturbations quand une di ou une trisubstitution se produisait dans les cycles A, B et/ou C.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—VIII*

THIOGLYCOLLIC ACID AS A MASKING AGENT

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Summary—The masking properties of thioglycollic acid (TGA) as well as the possibilities of its use in complexometry have been studied. It has been found that thioglycollic acid in an alkaline medium perfectly masks metals such as Pb, Bi, Cd, Ag, Hg, Zn, Tl, In and Sn because of the formation of colourless complexes. In this medium TGA forms intensely coloured complexes with Fe, Co and Ni. The red coloration of the Fe-TGA complex can be prevented by the addition of triethanolamine. It has been found that the Ni- and Co-EDTA complexes do not react with TGA. This enables a highly selective determination of nickel and cobalt to be made. Also, manganese can be determined in the presence of other metals screened with TGA. The advantages of TGA in comparison with potassium cyanide are discussed.

POTASSIUM cyanide is still a frequently used masking agent in complexometry, because it permits the direct complexometric determination of calcium and magnesium even in the presence of some divalent metals forming sufficiently stable complex cyanides. In view of its extreme toxicity, however, it ranks among the less popular reagents, particularly in routine analysis. In many countries its storage and consumption are under the control of various safety regulations so that large quantities of it in laboratories are not much favoured. Its replacement by an equally efficient, non-toxic and inexpensive reagent is desirable.

Some time ago certain substances were proposed to meet this emergency. Thus one can mention 2,3-dimercaptopropanol¹ which, however, on account of its price, was not introduced to any appreciable extent. Our experiments have revealed that of a number of substances the properties of which recommend them for use in complexometry, thioglycollic acid (TGA) is the most advantageous. Its main asset, compared with potassium cyanide, is the fact that in an alkaline medium it also forms colourless and soluble complexes with a number of other metals such as lead, bismuth, tin, *etc.* Further advantages are that it can be safely added even to acidic solutions and that, in using its neutralised solutions, the pH of the titrated solution is not essentially changed. In aqueous solutions it is sufficiently stable.

In masking of the accompanying cations the colour of the complexes formed is always of great significance. Although thioglycollic acid is well known as a sensitive colorimetric reagent for iron, with which it forms in an alkaline medium an intense red complex, a judicious choice of conditions (the presence of triethanolamine and sodium hydroxide) also makes it applicable to the masking of other elements even in the presence of iron. Like cyanide, it forms a colourless complex with copper in an alkaline medium.

* Part VII: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1961, 8, 743.

TABLE I. REACTIONS OF THIOGLYCOLIC ACID

Ion	Remarks
Ag	A yellow-white, gelatinous precipitate, insoluble in an excess of TGA, readily soluble in ammonia. Ammoniacal TGA also dissolves AgCN and AgI.
Hg	A white precipitate soluble in mineral acids and ammonia to give a colourless solution. The Hg-EDTA complex also reacts quantitatively with TGA.
Bi	A yellow-white precipitate, soluble in an excess of TGA as well as in ammonia to give a colourless solution. The Bi-EDTA complex reacts quantitatively with TGA both in an acidic and alkaline medium.
Cd	A white precipitate, soluble in an excess of reagent or in ammonia to give a colourless solution. Similar properties are observed with the Cd-EDTA complex.
Pb	A white yellow precipitate, soluble in ammonia. The EDTA complex reacts quantitatively also with TGA. $PbSO_4$ and $PbCrO_4$ are soluble in ammoniacal TGA.
Cu	First a brown solution, then a precipitate, changing on addition of further TGA to a yellow one, soluble in ammonia to give a colourless solution. The Cu-EDTA complex behaves similarly.
Tl	Masked in an acidic as well as alkaline medium. In acidic solution at higher concentrations of Tl a crystalline precipitate, soluble in ammonia, separates. The EDTA complex reacts similarly. (Possibility of determination of Th in the presence of Tl in an acidic medium-Xylenol Orange as indicator).
As, Sb	Without marked colour reactions.
Sn	A colourless complex in an alkaline medium.
Fe	In an acidic medium, a reduction, producing an unstable blue coloration, occurs first. Subsequently the solution becomes colourless, then turns intensely red on the addition of ammonia. In the presence of triethanolamine (TEA) and sodium hydroxide the solution is decolourised because of the formation of a TEA-complex. The Fe-EDTA complex is slowly reduced by TGA.
Cr, Al, Ti Th, Be	Without marked colour reaction.
Ni	The brown coloration developed in an alkaline medium disappears on the addition of EDTA. The Ni-EDTA complex does not react with TGA. (Possibility of determination of Ni in the presence of Cu, Zn, Cd, etc.)
Co	The yellow-brown to red-brown coloration developed in an alkaline medium does not change on the addition of EDTA. (Possibility of masking small amounts of Co in the determination of Ni.) The Co-EDTA complex does not react with TGA. (Possibility of determination of Co in the presence of Pb, Cu, Zn, etc.)
Mn	No reaction in an acidic medium. In an alkaline medium an unstable brown-yellow coloration develops, deepening on stirring and in contact with air. The addition of KCN produces an intense red coloration, becoming paler on standing but deepening on stirring and in contact with air. The presence of ascorbic acid gives no colour response. The Mn-EDTA complex does not react with TGA. (Possibility of determination of Mn even in the presence of TGA.)
Zn	A colourless complex in an alkaline medium. Perfect masking against EDTA.
In	A colourless complex in an alkaline medium. Also, the In-EDTA complex reacts with TGA.
Ga	Does not react with TGA at all. (Possibility of determination of Ga besides In.)
WO_4^{2-}	A slightly yellow coloration in an acidic medium even in the presence of EDTA. In an alkaline medium the coloration disappears.
MoO_4^{2-}	An intense yellow coloration in an acidic medium even in the presence of EDTA. In an alkaline medium the coloration disappears.
UO_2^{2+}	An intense red coloration in an alkaline medium even in the presence of EDTA.
Ca, Sr, Ba, Mg	Without colour reactions.

The study of the reactions of thioglycollic acid with metal ions in the presence of EDTA or DCTA (1,2-diaminocyclohexan-N,N,N',N'-tetra-acetic acid) has revealed still further advantages over potassium cyanide. For example, the EDTA complex with nickel or cobalt does not react in an alkaline medium with TGA, which permits a number of further, hitherto impracticable complexometric determinations, such as that of nickel in the presence of copper, zinc, iron, *etc.*, to be made. This preliminary communication presents a survey of the reactions of TGA with currently occurring cations with respect to the requirements of complexometry, and gives examples of some new determinations.

EXPERIMENTAL

Reagents

A 16% solution of thioglycollic acid was prepared from an 80% solution (produced by Lachema, Brno) by dilution with redistilled water (1:5). The solutions of the cations and of EDTA and DCTA were prepared in 0.05M concentrations from reagent-grade chemicals.

Orientation experiments

The orientation experiments, the results of which are presented in Table I, were carried out as follows: 5 to 10 ml of a 0.05M solution of the corresponding cation were diluted to about 50 ml, TGA added in portions and the changes in the solution observed. Subsequent to this the solution was neutralised with conc. ammonia solution and 20 ml added in excess. The same procedure was applied to reactions proceeding in the presence of an excess of EDTA and of DCTA.

A similar study has been made of the reactions of cations in the presence of DCTA, which, as is known, forms more stable complexes than does EDTA. As would be anticipated some DCTA complexes reacted with TGA only very slowly or not at all. Accordingly, the use of DCTA in combination with TGA is not recommended.

TABLE II. DETERMINATION OF Ni IN THE PRESENCE OF Cu, Cd, Pb, Zn AND Ag

Ni taken, <i>mg</i>	Other metal(s) taken, <i>mg</i>	0.05M EDTA, <i>ml</i>	0.05M CaCl ₂ , <i>ml</i>	Ni found, <i>mg</i>
14.26		10.00	5.14	14.26
14.26	(thioglycollic acid)	10.00	5.17	14.18
14.26	3.18 Cu	10.00	5.17	14.18
14.26	63.54 Cu	10.00	5.12	14.32
14.26	127.08 Cu	10.00	5.12	14.32
14.26	28.10 Cd	10.00	5.13	14.29
14.26	56.20 Cd	10.00	5.17	14.18
14.26	140.51 Cd	10.00	5.05	14.52
14.26	51.80 Pb	10.00	5.17	14.18
14.26	518.03 Pb	10.00	5.21	14.07
14.26	16.35 Zn	10.00	5.12	14.32
14.26	163.50 Zn	10.00	5.17	14.18
14.26	53.94 Ag	10.00	5.14	14.26
14.26	539.40 Ag	10.00	5.15	14.22
57.04	31.77 Cu, 28.10 Cd, 51.80 Pb 65.38 Zn	25.00	5.55	57.09
57.04	15.88 Cu, 28.10 Cd, 51.80 Pb 16.35 Zn, 269.50 Ag	25.00	5.55	57.09
57.04	15.88 Cu, 28.10 Cd, 51.80 Pb 65.38 Zn	25.00	5.52	57.15
5.70	31.77 Cu, 56.20 Cd, 103.60 Pb, 32.69 Zn, 107.88 Ag	10.00	7.95	5.96

Selective determination of nickel

As one of many cases presented in the above survey of reactions of TGA the possibility of the indirect determination of nickel in the presence of a number of elements has been studied. The procedure is based on a back-titration of an added excess of EDTA with calcium solution, to a Thymolphthalexone end-point.

Procedure: To an acidic solution of the cations (see Table II), TGA (1:5) is added in small portions or dropwise. This is accompanied by various colour changes depending on the composition of the solution. In the absence of copper the coloration is pure brown because of the formation of the Ni-TGA complex. If copper is present, there is a transient brown colour. With further addition of TGA a yellow precipitate appears. On the addition of 20 to 25 ml of conc. ammonia solution the precipitate dissolves and only the brown Ni-TGA complex remains. A slight excess of 0.05M EDTA solution decolorises it, the solution then being faintly blue because of the formation of the Ni-EDTA complex. The solution is diluted when necessary, Thymolphthalexone added and the excess of EDTA back titrated with 0.05M calcium chloride solution to an intensely blue coloration. Some results for this procedure are given in Table II.

Out of the other interfering elements the most likely to be encountered are aluminium and iron. The masking of aluminium by means of triethanolamine presents no difficulties. Iron, if the solution is not extremely alkaline, reacts with TGA to give an intense red coloration. However, if sufficient sodium hydroxide is now added, the solution becomes decolorised completely or remains only slightly yellow. This is because the increased alkalinity produces a quantitative formation of the Fe-TEA complex which does not interfere in the determination. Another advantage of TEA is that it prevents the separation of nickel hydroxide in the strongly alkaline medium.

For the determination of nickel in the presence of iron the above described procedure must be somewhat modified: To an acidic solution of nickel, copper, iron, aluminium and other heavy metals, add thioglycolic acid (1:5), in portions, to the disappearance of the brown coloration and to the formation of a bright yellow precipitate (Cu-TGA salt). On the addition of 20 ml of 20% triethanolamine the solution turns intensely red (Fe-TGA complex). Add 1M sodium hydroxide till the red coloration completely disappears (Fe-TEA complex). Now add a small excess of 0.05M EDTA solution and allow to stand for 3–5 min with occasional stirring. At this point the solution is generally too alkaline and it is, therefore, advisable to dilute it to 300–350 ml to eliminate interference from the bluish colour of the Ni-EDTA complex in the colour change of the indicator. The excess EDTA is titrated, as in the foregoing case, with 0.05M calcium chloride solution to an intense blue end-point using Thymolphthalexone as indicator. Some of the results are presented in Table III.

TABLE III. DETERMINATION OF Ni IN THE PRESENCE OF Fe, Cu AND Al

Ni taken, mg	Other metal(s) taken, mg			Ni found, mg
	Fe	Cu	Al	
2.85	13.97	317.7	13.49	2.93
28.52	2.79	15.89	13.49	28.78
28.52	13.97	158.85	26.98	28.69
14.26	2.79	158.85	13.49	14.28
14.26	8.38	158.85	13.49	14.36
14.26	13.97	15.89	26.98	14.35
57.04	8.38	158.85	13.49	57.23
57.04	27.93	317.70	—	58.54 ^a

^a End-point not sharp.

In a parallel study of the analysis of iron-chromium-nickel alloys² we have found that for a strongly alkaline medium the most suitable indicator is Fluorexon (calcein). The above described method can, therefore, be modified as follows: After making the solution alkaline with potassium hydroxide (not with sodium hydroxide³), add Fluorexon solution dropwise till the faintly blue solution turns pink, then titrate with calcium chloride solution to the appearance of a distinct green fluorescence. In this case the end-point is much sharper than with Thymolphthalexone.

Selective determination of manganese

Like nickel, manganese can also be determined if retained in the bivalent state by means of ascorbic acid (hydroxylamine hydrochloride is not sufficiently efficient in this case). The procedure is the same as the preceding one, except that 0.1–0.2 g of ascorbic acid is initially added to the solution to be analysed. Several results of the determination of manganese in the presence of other metals are given in Table IV.

TABLE IV. DETERMINATION OF Mn IN THE PRESENCE OF Fe, Cu AND Al

Mn taken, mg	Other metal(s) taken, mg			Mn found, mg
	Fe	Cu	Al	
5.39	13.97	15.89	6.75	5.38
13.47	13.97	158.85	13.49	13.56
26.95	2.79	31.77	26.98	27.01
53.89	13.97	317.70	6.75	53.90

Zusammenfassung—Die Maskierungseigenschaften von Thioglycollsäure (TGS) und ihr möglicher Gebrauch in der Komplexometrie wurden studiert. Es wurde gefunden, dass TGS unter Bildung farbloser Komplexe die nachfolgenden Elemente in alkalischem Medium vollständig maskiert: Pb, Bi, Cd, Ag, Hg, Zn, Tl, In und Sn. In alkalischem Medium werden intensiv gefärbte Komplexe von Fe, Cu und Ni gebildet. Die Bildung des roten Eisenkomplexes kann durch Zusatz von Triäthanolamin verhindert werden. Die ÄDTE-Komplexe von Ni und Co reagieren nicht mit TGS, was eine hochselektive Bestimmung der beiden Metalle ermöglicht. Mangan kann in Gegenwart anderer Metalle bestimmt werden, wenn letztere mit TGS maskiert sind. Die Vorteile von TGS gegenüber Kaliumcyanid werden diskutiert.

Résumé—Les auteurs ont étudié les propriétés complexantes de l'acide thioglycollique (TGA), ainsi que les possibilités de son utilisation en complexométrie. Ils ont trouvé que l'acide thioglycollique dissimule complètement en milieu alcalin des métaux comme Pb, Bi, Cd, Ag, Hg, Zn, Tl, In, Sn par formation de complexes incolores. Dans ce milieu, le TGA forme des complexes colorés de façon intense avec le fer, le cobalt et le nickel. La coloration rouge du complexe Fe-TGA peut être évitée par addition de triéthanolamine. Par la suite, les auteurs ont trouvé que les complexes Ni-EDTA et Co-EDTA ne réagissent pas avec le TGA. Cela permet un dosage extrêmement sélectif du nickel et du cobalt. Le manganèse peut aussi être dosé en présence d'autres métaux complexés par le TGA. L'avantage du TGA par rapport au cyanure de potassium a été discuté.

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PHOTOMETRIC TITRATIONS—V*

A SELECTIVE, CHELOMETRIC DETERMINATION OF COBALT

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Summary—Cobalt can be titrated with good selectivity by converting it with hydrogen peroxide in alkaline medium to the cobalt^{III} EDTA complex and back-titrating photometrically in acid medium the excess EDTA with bismuth solution, using pyrocatechol violet as indicator. No interference is observed with alkalis, alkaline earths, Ni, Cu, Cd, Zn, Pb, Al, U, and W. Bi, Zr, In, Ga and other ions forming very stable EDTA complexes are co-titrated. Mo, Fe, Ag and Hg interfere and should be separated. The interference of Mn can be excluded by addition of ascorbic acid. Th can be masked with sulphate. Cr^{III} is co-titrated, but by applying a difference method operating with two aliquots, both Cr and Co can be determined. Complexing anions interfere, as does chloride, which causes a turbidity with bismuth.

A PARTICULAR chelometric determination of cobalt using the element in its trivalent state has been described by Kinnunen and Wennerstrand.¹ Cobalt in ammoniacal solution is oxidised with hydrogen peroxide in the presence of EDTA. The solution is then acidified to pH 2 and the excess of EDTA is back-titrated with standard thorium solution using xylenol orange as indicator. Only small amounts of cobalt can be titrated using this procedure because the very intense red colour of the cobalt^{III} EDTA complex readily obscures the end-point. A photometric end-point should improve the method considerably. Thorium, however, is not the best choice for the back-titration, for several reasons, and the present authors have investigated the use of bismuth for this purpose employing pyrocatechol violet as indicator.

This titration is possible even at very low pH values,² where most of the other metals do not react with the indicator and where the apparent stability constants of their EDTA complexes are so low that the metal ions are readily replaced by bismuth. The replacement reaction, however, is slow in some cases (nickel and to some extent copper); hence it is better to complex with bismuth the EDTA which is in excess over the cobalt, thus hastening the replacement, and then to titrate the excess bismuth with EDTA. There is no danger that any cobalt^{III} might be replaced, even after prolonged standing with excess bismuth, because the Co^{III}Y complex was estimated to have a very high stability constant ($\log K = 40.7$).³ Back-titrations with bismuth have successfully been used for the determination of various metal ions,⁴ and the method was especially useful for a selective visual titration of nickel where nickel was frozen in the EDTA complex by lowering the temperature of the solution to nearly 0°.⁵

Photometric determination of the end-point

The absorbance curves of pyrocatechol violet and its bismuth complex at various pH values are shown in Fig. 1. From these curves it can be deduced that even at pH 0.5 a sufficient difference between the absorbances of the two species exists at a

* Part III—*Talanta*, 1961, 8, 720.

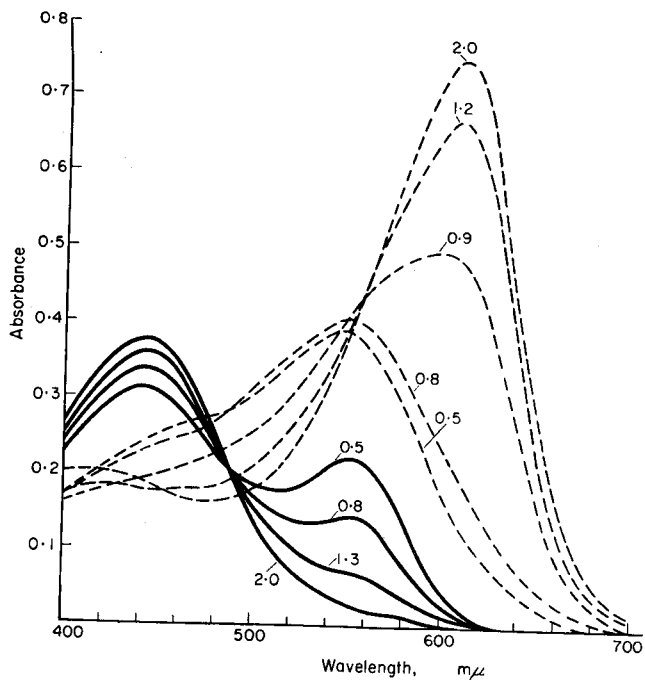


FIG. 1.—Absorbance curves of pyrocatechol violet (solid line) and its bismuth complexes (dotted line) at various pH values.

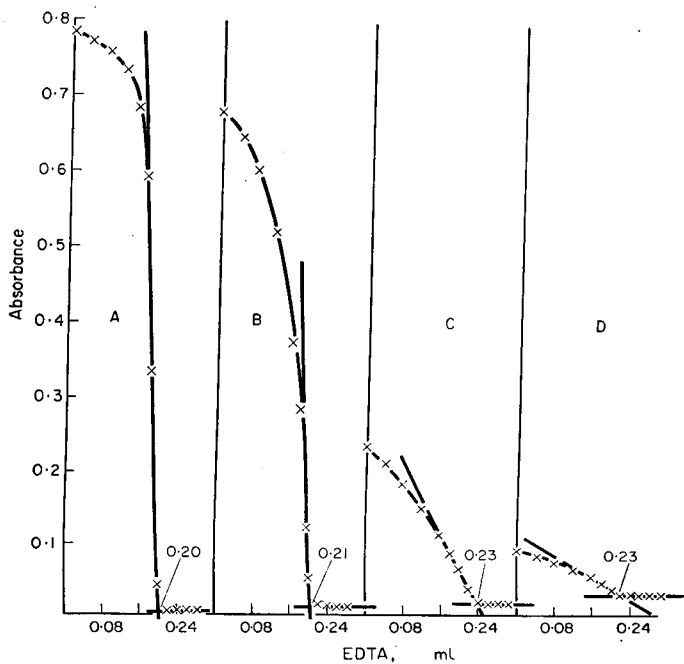
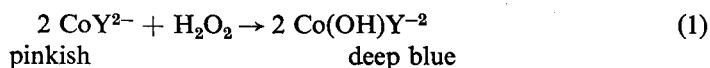


FIG. 2.—Photometric titration curves near the end-point of bismuth with EDTA, using pyrocatechol violet as indicator at various pH values. Curves A to D are for pH 2.0, 1.5, 1.0 and 0.5 respectively.

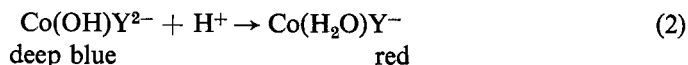
wavelength of about 600 to 620 $m\mu$ to provide the condition for a suitable photometric end-point. Experimental determination of the titration curves at various pH values are shown in Fig. 2. The precision is within the limits to be expected.

The cobalt^{III} EDTA complex

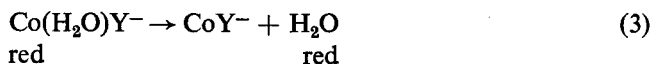
It is known that there are two red complexes, which do not appear very different in colour to the eye, but which may be distinguished by a phototitrator. The cobalt-EDTA complexes have been studied by Schwarzenbach.⁶ In alkaline medium the oxidation of the cobalt^{II}-EDTA complex by hydrogen peroxide proceeds, according to Schwarzenbach, in the following manner:



On acidification a proton is attached, this process being accompanied by a colour-change to red:



The complex containing one molecule of co-ordinated water is not stable, and it dissociates in a rather slow process according to the equation



The absorbance curves of both complexes are shown in Fig. 3. Fortunately the two curves are identical at the wavelength selected for the titration, hence there will be no interference from this process.

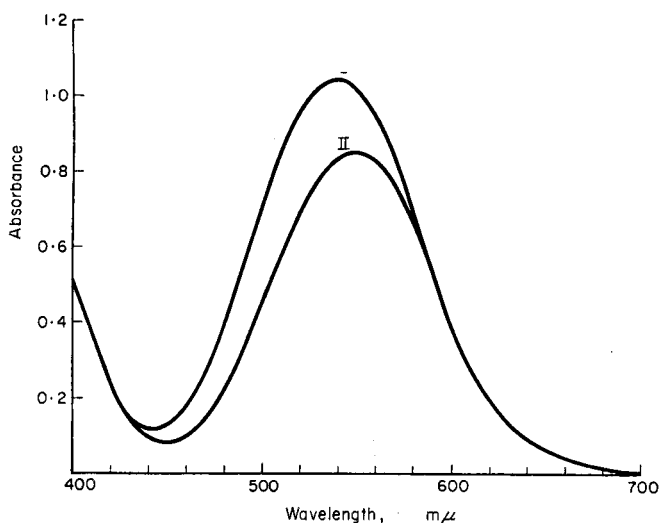
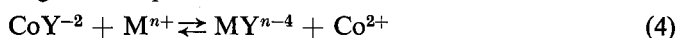


FIG. 3.—Absorbance curves of the complexes $\text{Co(H}_2\text{O)Y}^{-}$ (I) and CoY^{-} (II) at pH about 1.8.

Kinnunen and Wennerstrand¹ performed the cobalt oxidation in an ammoniacal medium. This, however, has been found to be inconvenient for the present purpose because the hydrogen peroxide oxidises the ammonia to nitrogen. This results in

the formation of a large number of small bubbles which are difficult to remove, and which can interfere with the response of the phototitrator. The solution was therefore made basic with sodium hydroxide solution. A smaller amount of oxidant suffices for complete oxidation of the cobalt, and barely any bubbles are produced. In addition, the rate of the oxidation reaction seems to be greatly enhanced. In consequence of these findings it seems to be more realistic to write reaction (1) in a modified form involving the hydroxo complex of the cobalt^{II} EDTA. In alkaline medium above pH 10 the colour is no longer the clear pink of the complex CoY^{-2} as present in neutral solution.

A study of the oxidation mechanism revealed that only the cobalt^{II} which is complexed by EDTA is rapidly oxidised. Hence the addition of EDTA which represents an excess with respect only to the amount of cobalt present is not adequate when other metal ions are present (except alkali metals). A partial replacement of cobalt^{II} may occur according to the equation



How far this equilibrium will be shifted towards the right depends on the concentration of M and on the ratio of the stability constants of the complexes involved. Even with a metal like magnesium, which has a low stability constant, the shift is sufficient to cause low results in the cobalt determination when a portion of the magnesium remains uncomplexed.

EXPERIMENTAL

The phototitrator described in a previous paper of this series was used.⁷ The titrations were performed in rectangular cells having a 1.5- and 3-cm lightpath and 100- or 200-ml capacity. An interference filter, 622 m μ , was used. Metal and EDTA solutions were prepared from reagent-grade material and standardised according to well established chelometric procedures. The absorbance curves were made with a Cary Model 14 Recording Spectrophotometer. An approximately 0.2% aqueous solution of pyrocatechol violet was used.

Procedure

Add a measured amount of standard EDTA solution to the sample so that all metal ions present (except the alkalis) are complexed and some EDTA is present in excess. Add 2*N* sodium hydroxide solution dropwise while stirring until a pH of about 11 is reached. Add 4–5 drops of 30% hydrogen peroxide and stir. Add concentrated nitric acid dropwise, until the desired pH is reached (0.5–2) depending on the composition of the sample. Add a spatula-tip full of urea and stir. Add several drops of indicator solution (more than would be used for a visual end-point) and adjust the titrator so that about 90% T is read.*

Add an exactly measured amount of bismuth standard solution at least equivalent to the EDTA present. Titrate the free bismuth with standard EDTA. Near the end-point add small increments of titrant only. Plot ml of titrant on the abscissa (linear) and transmittance readings on the ordinate (logarithmic) using semilog paper. Evaluate the graph to find the end-point in the usual manner.

Calculation: Let A be the total number of ml of EDTA added (before the oxidation step and during the final titration), and B the ml of bismuth solution added. Then the calculation is based on the following formula, where M is the molarity of the solution indicated by the subscript:

$$(A \times M_{\text{EDTA}} - B \times M_{\text{Bi}}) \times 58.94 = \text{mg of cobalt.}$$

Study of interferences

No interference was observed through oxidation of EDTA by the moderate amounts of unreacted hydrogen peroxide at pH 10–11. Similarly at pH 0.5 no reaction

* Adjustment to 100% T is not recommended because sometimes the final transmittance reading is higher than the initial one. Thus the above procedure provides some sort of a safety range.

was noticeable; at least not during the time required to complete the analysis. Even in the presence of considerable amounts of ascorbic acid the cobalt^{III} EDTA complex is not reduced in acid medium. It is known² that the oxides of nitrogen present in nitric acid will react with pyrocatechol violet, thus causing a very rapid drift of the galvanometer. Hydrogen peroxide left over from the oxidation step oxidises the nitrogen oxides and thus eliminates the interference; it does not attack the indicator. Urea serves equally well for eliminating this kind of interference.

The oxidation of cobalt^{II} EDTA is slower at $\text{pH} < 10$. Hence it is important that the pH be adjusted to a value greater than 10 so that complete oxidation is assured without undue prolongation of the procedure.

The following ions do not interfere at a pH of 2 or lower: alkalis, alkaline earths, Ni, Cu, Zn, Cd, Pb, and UO_2^{+2} .

Aluminium is only very slowly and incompletely replaced at pH 2 but no interference occurs at pH 0.5–0.7. Thus cobalt may be titrated in the presence of these elements without any masking procedures.

Manganese is also oxidised to an Mn^{IIIY} complex which interferes. The complex, however, can readily be reduced by ascorbic acid. It is important to add this reductant after acidification of the oxidised solution and just before the addition of the indicator.

If the solution containing chromium^{III} and cobalt is treated according to the normal procedure chromium interferes. Results for cobalt determinations are found to be high, indicating that some of the chromium is being co-titrated. Chromium forms its EDTA complex very slowly, so that it is precipitated during the alkalisation step. Some of the chromium is converted to chromate when hydrogen peroxide is added to the alkaline solution. When the solution is acidified the precipitated chromium hydroxide redissolves. Any dichromate present would not interfere *per se*; but in the presence of some remaining unreacted hydrogen peroxide in acid medium it is reduced to chromium^{III} which *in statu nascendi* complexes with EDTA at once. If, however, the solution containing chromium and EDTA is heated at a pH of 2–3, the deep violet chromium^{III} EDTA complex is formed. Any excess EDTA can now be titrated with bismuth solution even at pH values as low as 0.5–0.7. This titration gives chromium alone since the cobalt is present in the bivalent state and is readily replaced by bismuth. In a second aliquot the sum of cobalt and chromium can be determined if the analogous modification of the procedure is followed, *i.e.*, heating the sample with excess EDTA to hasten the complexation of chromium and then making the cooled solution alkaline and oxidising the cobalt with hydrogen peroxide and proceeding as before. Cobalt is then obtained by difference. Unless the acidification of the solution is performed immediately after the oxidation a small amount of chromium may be converted into chromate. In order to reduce this amount rapidly, the addition of a few crystals of ascorbic acid is recommended after the acidification.

Thorium forms a highly stable EDTA complex and hence will be co-titrated. However, the addition of sulphate lowers the apparent stability constant sufficiently to prevent interference. If this masking procedure is applied, the final titration has to be performed at pH about 0.5 in order to avoid the formation of a turbidity on the addition of the bismuth solution.

All metals with a high stability constant for the EDTA complex will be co-titrated, *e.g.*, bismuth, zirconium, indium and gallium (see reference 4) Mercury causes

peculiar time effects and silver is precipitated as oxide at the high pH; it has in addition a catalysing effect on the oxidation of EDTA by hydrogen peroxide, and also speeds the decomposition of the latter. Sometimes a rather violent reaction occurs. Thus both elements should be separated before the cobalt determination.

Iron was already noted in a previous paper⁴ as a source of interference. Theoretically it should be co-titrated, as deduced from the high stability of its EDTA complex. In addition, it attacks the indicator and renders the titration impossible. Iron must therefore be absent.

Anions interfere if they exhibit complexing properties, e.g., iodide, citrate, tartrate and fluoride. Chloride, even at pH 0.5 causes a turbidity with bismuth when present in more than trace amounts. Molybdate interferes by blocking the indicator. Tungstate, however, has no influence on the determination.

CONCLUSIONS

As can be seen from some representative results presented in Table I, the accuracy and precision of the method are satisfactory. It is unfortunate that no method could be found to exclude the interference of iron, because it is so frequently allied with cobalt. A previous separation helps but increases the time element in any analysis. The method will, however, give quick and reliable results in the presence of various other metal ions, especially in the presence of nickel and copper.

TABLE I. DETERMINATION OF COBALT IN PURE SOLUTIONS AND IN PRESENCE OF THE FOREIGN METALS

0.1M solution of foreign metal added, ml	Titration at pH	0.1000M EDTA, ml		
		Calculated	Required	Difference
None	0.6	4.49	4.47	+0.02
None	1.0	9.25	9.21	-0.04
None	1.0	18.42	18.50	+0.08
None	1.5	23.40	23.56	+0.16
Th, 5 (20 of ml 0.1 M Na ₂ SO ₄ for masking)	0.6	5.20	5.24	+0.04
Mn, 5	0.6	4.60	4.63	+0.03
UO ₂ ²⁺ , 5	0.7	5.63	5.66	+0.03
WO ₄ ⁻² , 2	0.6	5.67	5.60	-0.07
Ni, 5	0.6	4.58	4.59	+0.01
Ni, 15	0.6	8.56	8.57	+0.01
Ca, 5; Mg, 5	0.6	4.26	4.26	±0.00
Cu, 15	1.5	5.79	5.78	-0.01
Cu, 5; Ni 10	0.6	7.10	7.08	-0.02
Al, 20	0.6	5.32	5.34	+0.02
Ni, 9; Zn, 5; Pb, 8; Cu, 5; Mg, 5	0.6	8.89	8.90	+0.01

The possibility of determining both cobalt and nickel in the same sample by combining the new approach with the method published previously⁵ is of special interest. The sample is treated according to the procedure described in the present paper but cooled to 0° by adding ice. Then the back-titration is performed with bismuth, thus giving the sum Ni + Co. The temperature is then raised to room temperature and nickel is replaced by addition of bismuth, the excess of which is

titrated with EDTA, thus giving the value for cobalt. The disadvantage of this procedure is that water condenses from the surrounding air on the cell containing the cooled solution. It is necessary to position the cell free, between the lamp housing and the photo-receptor compartment (see reference 7), and to wipe it dry when the end-point region of the titration curve is recorded. Silicone treatment and operating in a dehumidified room help greatly.

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Zusammenfassung—Eine Methode zur gut selektiven Bestimmung von Cobalt wird beschrieben. Cobalt wird mittels Wasserstoffperoxyd in alkalischem Medium zum Cobalt(III) ÄDTE-Komplex oxydiert. Nach Ansäuern wird der Überschuss von ÄDTE mit Wismutlösung photometrisch zurücktitriert unter Verwendung von Brenzkatechinviolett als Indicator. Alkalimetalle, alkalische Erden, Cu, Ni, Zn, Cd, Pb, U, Al und W stören nicht. Bi, Zr, In, Ga und andere Metallionen, die sehr stabile ÄDTE-Komplexe formen, werden mittitriert. Mo, Fe, Ag und Hg stören und müssen vorher abgetrennt werden. Die Störung von Mangan wird durch Zusatz von Ascorbinsäure behoben, während Th mit Sulfat maskiert werden kann. Cr(III) wird mittitriert. Durch Anwendung eines Differenzverfahrens und operieren mit zwei aliquoten Lösungsteilen lassen sich aber sowohl Cr als auch Co bestimmen. Komplexbildende Anionen wie Jodid, Citrat, Tartrat oder Fluorid stören. Gleichfalls stört Chlorid (wenn mehr als in Spuren anwesend) durch Bildung einer Trübung mit Wismut.

Résumé—Le cobalt peut être dosé avec une bonne sélectivité en le transformant à l'aide d'eau oxygénée en milieu alcalin en complexe cobalt(III)-EDTA; l'excès d'EDTA est dosé en retour, par photométrie, en milieu acide par une solution de bismuth avec le violet de pyrocatechol comme indicateur. Aucune interférence n'a été observée avec les alcalins, les alcalino-terreux, Ni, Cu, Cd, Zn, Pb, Al, U et W. Bi, Zr, In, Ga et les autres métaux formant des complexes très stables avec l'EDTA sont titrés en même temps. Mo, Fe, Ag et Hg gênent et doivent être séparés. L'interférence de Mn peut être éliminée par addition d'acide ascorbique. Th peut être masqué par du sulfate. Cr(III) est titré avec le cobalt, mais en appliquant une méthode différente effectuée avec deux parties aliquotes, Cr et Co peuvent être dosés tous les deux. Les anions complexants gênent, de même que le chlorure qui produit un trouble avec le bismuth.

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ANALYSIS OF GASES AND VAPOURS BY SPECTROSCOPIC TECHNIQUES—I

EMISSION SPECTROSCOPY

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Summary—Theoretical and experimental aspects of the analysis of gases and vapours by emission spectroscopy are discussed and the current literature on molecular emission spectroscopy is reviewed.

At the present time a great deal of information is available on the electronic molecular spectra of a large number of gases and vapours, but surprisingly few applications of such spectra to analytical problems have been described in the literature.

The analysis of mixtures of inert and/or permanent gases is often not easy to achieve using techniques in which the constituents are individually isolated and identified. Of the methods available which do not require preliminary separation of the components of a mixture, those employing a spectroscopic technique are intuitively very attractive, since the manner in which any particular gas or vapour interacts with electromagnetic radiation is characteristic of that substance. The frequency of radiation used can vary from radio frequencies to the extreme ultraviolet. So far, almost all of the published work relates either to the infrared or to the visible and ultraviolet, and most effort has been applied to the study of absorption spectra of substances in the liquid phase.

The aim of this series of papers is to review the available data that have accumulated on the emission and absorption spectra of gases and vapours and to discuss the possible analytical applications of these data. For convenience, the study has been divided into three parts. The first part deals specifically with emission spectroscopy; the second part reviews the absorption of ultraviolet and visible radiations by gases; in the third part of the series some experiments on the analytical application of vapour absorption spectra are described.

EMISSION AND ABSORPTION SPECTROSCOPY

Spectroscopic transitions giving rise to emission and absorption of radiation in the visible or ultraviolet involve a change from one electronic energy level to another. This is the fundamental difference between electronic spectra and infrared spectra, which arise from changes in vibrational and rotational energy only. For a molecule, the electronic transition is necessarily accompanied by simultaneous changes in vibrational and rotational energy, giving rise to band spectra, as distinct from the line spectra given by atoms.

Spectra can be classified into two broad categories, (a) emission spectra and (b) absorption spectra. Molecular emission spectra arise because some of the molecules

of the system have been excited by physical or chemical means to an electronic level above the ground state. When these molecules revert to the ground electronic state, the excitation energy is given out as electromagnetic radiation. The relationship between initial and final energies (E_1 and E_2) and the frequency of radiation emitted (ν) is the well known one

$$E_1 - E_2 = h\nu \quad (1)$$

where h is Planck's constant.

Molecular absorption spectra arise from the converse process. When a beam of electromagnetic radiation is allowed to pass through a material, some of the frequencies in the beam are removed, *i.e.*, they are absorbed by the material. Those frequencies which are removed again must satisfy the quantal relationship (1), which means that the frequencies absorbed correspond to the energies required to raise the molecules from their ground electronic states to some excited states.

In order to obtain an emission spectrum from any substance it is first necessary to supply energy to the molecules to promote a proportion of them to excited electronic states. This can be done in a variety of physical ways, such as bombardment with high-speed electrons or ions, excitation of a gas in a discharge tube, or the use of an electric arc. Excitation may also be accomplished by chemical means, whereby the excitation energy is supplied as heat given off from an exothermic reaction. This is the case in emission from flames and explosions. The advantages and disadvantages of the various methods of excitation will be discussed later in this paper.

The technique of absorption spectroscopy is, on the whole, simpler than that of emission spectroscopy. In essence one requires only a suitable cell to contain the gas or vapour, having end-windows of quartz for work in the near ultraviolet, or of lithium fluoride for the extreme ultraviolet, together with a source of continuous radiation. The latter is usually a gas discharge lamp using hydrogen or xenon. The spectrograph or spectrophotometer used to detect the absorption is the same as that used in emission work.

Although the emission and absorption of radiation by a gas relates to transitions between the same electronic energy levels, the superficial appearance of the two types, and the regions in which they appear, may be quite different, for reasons given later in this review. For this reason, the proper interpretation of spectra requires a certain amount of experience, which militates against spectroscopic methods as routine analytical procedures.

Both methods are in a way complementary, in the sense that in some cases it is easier to obtain one type, in other cases the other. For instance, molecular oxygen only begins to absorb radiation below 2000 Å, which makes it very difficult to obtain a spectrum with instruments readily available in the laboratory, whereas the emission spectrum appears in the region 4000–6000 Å, and can readily be obtained using an ordinary quartz spectrograph.

From the analytical standpoint there are two ways in which the electronic spectra can be used, *i.e.*, qualitatively and quantitatively. The qualitative identification of a gas or the components of a gas mixture merely requires that one can positively ascribe a number of bands appearing at certain wavelengths to a particular substance. Because of the complexity of many spectra this often limits the type of mixture that one can analyse with certainty. On the whole, absorption spectra are less complex than emission spectra, and this favours the absorption technique in many cases.

Quantitative analysis requires one to be able to analyse qualitatively as an initial step, and then to be able to relate the intensity of either emission or absorption to the concentration of the gas. The theoretical and practical limitations here are more severe in the case of emission work. For example, the concentration of excited species giving rise to an emission spectrum depends on the means of excitation, the pressure of the gas, and the nature of the other gases present. An absorption spectrum, on the other hand, is usually independent of the nature of other gases present, and depends only on the constancy of the source giving the continuum. As mentioned previously, however, it is not always possible to obtain an absorption spectrum, and it then becomes necessary to use the emission technique even though the difficulties are greater.

THEORY OF EMISSION SPECTROSCOPY

The theoretical interpretation of the emission spectra of diatomic molecules is now well established,¹ and good progress has recently been made in providing a theoretical basis for the interpretation of the spectra of more complex molecules, particularly those which contain one or more aromatic rings.²

It is not proposed to attempt any comprehensive treatment of the theory in this review, but to outline some of the more important principles which are essential to the proper application of the technique of emission spectroscopy to gas and vapour analysis.

Atomic line spectra

The emission spectrum of an atom consists of a series of lines, each of these lines being associated with a transition from one electronic energy level to another. The line spectra of nearly all the elements in the periodic table have been investigated very thoroughly, and are tabulated in various reference books.^{3,4} The use of such spectra for analytical purposes has become widespread in the field of metal and alloy analysis, where the sample is volatilised in an arc and the emission spectrum is photographed. This can be followed by plate photometry to give quantitative results of good accuracy. Within the scope of this review, *i.e.*, that of gas and vapour analysis, the only gases giving rise to such line spectra are the inert gases He, Ne, Ar, Kr, Xe and Rn. Spectroscopic analysis for these gases should therefore be amenable to the same type of treatment as that used for metal analysis, apart from the method of excitation used.

In order to utilise the emission spectrum of an inert gas for quantitative analysis it is necessary to relate the intensity of one or more of the atomic lines to the amount of gas present in the system. The methods used to measure spectral intensity, and the difficulties inherent in these measurements, will be outlined in another section. For the moment we shall assume that such intensities can be measured accurately. The intensity of a given line, resulting from a transition between two electronic states, depends on the nature of the initial and final states. If we consider a system of atoms in which a certain proportion of the atoms has been excited from a low energy level, E_1 (say the ground electronic state), to a state of higher energy, E_2 , then transitions in which the excited atoms drop to the ground state, emitting radiation, will give rise to a line of frequency ν given by

$$\nu_{1,2} = \frac{E_2 - E_1}{h} \quad (2)$$

The rate of emission of this frequency $\nu_{1,2}$ is obviously dependent on the number of atoms involved in the transition per second. If we denote this number by $K_{1 \rightarrow 2}$, we can write for the intensity of the line of frequency $\nu_{1,2}$

$$I = A \cdot K_{1 \rightarrow 2} \cdot h \cdot \nu_{1,2}, \quad (3)$$

where A is a constant and h is Planck's constant.

$K_{1 \rightarrow 2}$ is determined by the time an atom remains in the excited state, called the mean life, which is inversely proportional to the transition probability. We can define the transition probability as the average number of transitions per second of an atom, giving this the symbol $P_{1,2}$ for the transition between states 1 and 2. Then if we have n atoms in the excited state, 2, it follows that

$$K_{1 \rightarrow 2} = n \cdot P_{1,2} \quad (4)$$

Combining equations (3) and (4) we obtain

$$I = A \cdot n \cdot P_{1,2} \cdot h \cdot \nu_{1,2} \quad (5)$$

In this equation, A is dependent on the actual experimental conditions, e.g., the type of excitation employed, which can be standardised. $P_{1,2}$ and $h\nu_{1,2}$ will be constant for one particular line. The number of atoms in the excited state, n , will, however, depend on a variety of factors, and in order to put emission spectroscopy on a really quantitative basis these factors must be taken into consideration.

It is obvious that for a given type of excitation, n will depend on the pressure of the gas, since the higher the pressure the more collisions each atom will suffer in unit time. This means that more excited atoms will lose their excitation energy in collision processes, without radiating, than at lower pressures, and hence the intensity of radiation will be less. This phenomenon is easily illustrated practically with a leak tester. At low pressures a gas can be easily made to luminesce, but as the pressure is increased the luminescence progressively decreases until it is totally extinguished. At this point all the excited atoms are being de-activated in radiationless collision processes.

The number n will also depend on the nature of the other gases present. The energy transfer process involved in a collision between an excited atom and a second atom or molecule, resulting in the excited atom losing its energy without radiating, will depend on the nature of this second species. Different molecules vary greatly in the ease with which they can remove electronic excitation from other molecules. If a gas is present which is more efficient at removing the excitation than the gas being excited, then the intensity of emission will be much less than it would be if this gas were absent, at the same total pressure. The converse applies if the foreign gas is less efficient than the parent gas at removing electronic excitation. In this case the emission intensity is greater than for the pure gas.

From the foregoing remarks it is evident that certain restrictions are operative in the use of spectral intensities as a measure of gas concentration. Because of these, any measurement of intensity must be of a comparative nature, since the absolute intensity depends both on the total pressure and on the nature and amount of other gases present.

Molecular band spectra

We shall first consider the emission spectrum of a diatomic molecule. Under low resolution the spectrum appears to consist of a series of bands, instead of the lines which occur in an atomic spectrum. With greater dispersion and higher resolution each of these bands is found to be a group of fairly closely packed lines. This difference between the atomic and molecular spectra results from the fact that whereas an atom has only one means of taking up energy in quantised units, *i.e.*, by changing its electronic configuration, a diatomic molecule has three, the extra two being its vibrational and rotational degrees of freedom. Each electronic transition, which would give rise to one atomic line, therefore gives in the case of a diatomic molecule a series of bands, the gross structure of the band system being determined by the associated changes in vibrational energy, and the fine line structure of each band arising because of simultaneous changes in the rotational energy.

The emission spectrum of a diatomic molecule can be used in the same way as an atomic spectrum for the qualitative identification of gases, by measurement and comparison with the existing data on gases. For this purpose the measurements usually made, and reported in the literature, refer to the so called band heads. Nearly all the bands in the spectra of diatomic molecules have the appearance of being sharp at one end and gradually fading away at the other end. The direction in which the band fades away to longer or shorter wavelengths is termed the direction of degradation. We therefore speak of bands being degraded to longer wavelengths (to the red), or to shorter wavelengths (to the violet). For purposes of qualitative identification it is therefore usually sufficient to measure the wavelengths of as many band heads as possible of the unknown spectrum, and to find which emitter gives bands corresponding to these, with the same direction of degradation.

The use of the emission spectrum of a diatomic molecule for quantitative analytical purposes involves considerably greater theoretical difficulties. Strictly speaking, one would require spectroscopic equipment capable of giving sufficient dispersion and resolution to isolate several of the rotational lines of a band, free from overlap with other lines. Designating the intensity of a single rotational line of frequency ν as I , the following relationship can be derived:

$$I = A \cdot P \cdot \nu^4 \cdot \exp(-E_{\text{rot.}}/kT) \quad (6)$$

where A is a constant dependent on the total intensity which will depend on the method of excitation and experimental set-up, P is the transition probability, $E_{\text{rot.}}$ is the rotational energy, k is the Boltzmann constant and T is the temperature in $^{\circ}\text{K}$.

The considerations discussed previously in relation to the use of atomic line spectra for quantitative analysis will apply here, notably the effects of total pressure and foreign gases on the number of de-activating collisions, resulting in radiation loss.

In many cases large dispersion and resolving power are not available, and in these circumstances it would seem obvious to use the band head intensity as a measure of concentration. For this practice small dispersion is actually preferable, since it crowds the rotational lines closer together at the head. The main theoretical objection to the use of the band head for this purpose is that the rotational line structure which forms the head is markedly dependent on the temperature of the system. From equation (6) it can be seen that I is proportional to $e^{-E_{\text{rot.}}/kT}$. The temperature T will in turn be dependent on the total pressure, on the nature of any other gas present,

and on the nature of the excitation. For instance, the rotational temperature of a gas in an electric arc will be much higher than for the same gas in a condensed discharge, resulting in a more complex rotational structure.

Band spectra from polyatomic molecules are necessarily more complex than diatomic molecular spectra. Except in a few cases, there is little regularity in the grouping of the bands, and in general the rotational structure cannot be resolved except with instruments of great resolving power such as large grating spectrographs. Although the theory of polyatomic spectra is now fairly well advanced, it is not nearly as complete as could be desired. This does not, however, prevent one from using the available literature on the recorded spectra of gases as a means of qualitative analysis. Since many polyatomic molecules give rise to headless bands or patches of continuous emission, the use of such spectra for quantitative analysis is much more restricted than in the case of diatomic spectra. Another difficulty encountered here, which will be discussed later, is the fact that in many cases polyatomic molecules tend to dissociate under the excitation conditions necessary to obtain an emission spectrum.

EXPERIMENTAL METHODS OF OBTAINING SPECTRA

(a) *Methods of excitation*

The various methods of excitation can be divided into four broad groups, which will be considered individually.

(i) *High-frequency discharges.* One of the first methods to be employed utilised the Tesla coil.⁵ The Tesla coil produces a high-frequency alternating output of about 50 kV, by means of a mechanical vibrator. Under the influence of such an HF alternating field, free electrons in a gas can acquire sufficient energy to excite and ionise gas molecules, and when the field is sufficiently strong the ionisation process becomes cumulative, leading to a breakdown in the insulating properties of the gas and the production of a luminous discharge. At low frequencies the breakdown process is substantially the same as that found in d.c. discharges, except that since the field is alternating the drift current does not transport electrons away from the space between the electrodes. This results in a simplification of the spectra obtained from a Tesla or any other HF discharge, compared with those obtained using d.c. discharges.

In practice the alternating field is usually applied between a central insulated electrode in the gas to be excited, and the outer wall of the container. Since there are no actual metallic conductors in contact with the gas, there are no lines arising from the metal atoms of the electrodes in the spectra obtained. This is an additional attractive feature of the method.

Two other methods of obtaining HF discharges in gases are extensively used in emission spectroscopy. They are known as the ring discharge and the valve oscillator discharge.⁶ In the first of these methods a conventional LC circuit, *i.e.*, one containing an inductance and a capacitance, is used in conjunction with a condensed spark to produce damped oscillations. The inductance is actually wound on the glass or quartz vessel used to contain the gas sample. The strength of the discharge can be controlled by varying the size of the spark gap; and by progressively increasing the strength, the spectra emitted can be made to change from the molecular band type to the line spectra of neutral atoms and ionised atoms.

In the valve oscillator discharge a triode valve is used to maintain continuous radio-frequency oscillations in a tuned circuit. A vessel containing gas at low pressure

may be made to emit radiation by application of this RF power to electrodes within the gas or wound on the outside of the vessel.

All of the methods described give essentially the same type of spectrum and they provide a useful method of obtaining emission spectra free from extraneous lines caused by metallic conductors.

(ii) *Discharge tubes*.^{5,6} If a tube having metallic electrodes at each end is filled with a gas, and connected to a source of d.c., then as the pressure of gas is gradually decreased, there comes a stage when the insulation of the gas breaks down and the tube acts as a conductor of electric current. At this stage the gas in the tube also begins to glow, the brilliance of the glow depending on the voltage and current being employed at any particular gas pressure. Different regions of the glow have been distinguished by various workers in this field, and some are more luminous than others. The brightest parts, and therefore the most useful for spectroscopic purposes, are known as the positive column and the negative glow.

The excitation process in the positive column the collisions of electrons with gas molecules, and the spectra obtained are predominantly caused by uncharged atoms and molecules. The spectra are however more complicated in appearance than those obtained from high-frequency sources for two reasons. One is that the number of excited electronic states reached in the column is much greater than in the case of the HF discharge, resulting in the appearance of more molecular band systems; and the second is that a considerable amount of decomposition of the gas occurs, leading to the appearance of spectra originating in the molecular fragments produced. Reduction of gas pressure and increase of field intensity both result in higher degrees of excitation.

In the negative glow region, excitation is caused by collisions with electrons from the direction of the cathode; and as a result of this the spectra obtained largely originate from positively charged ions. In order to take full advantage of this region a special type of discharge tube must be used, known as a hollow cathode tube. In this, the cathode is a cylinder and the radiation emitted is almost exclusively from the glow inside this cylinder. Spark lines of the metal used for the cathode are found in the spectra from such tubes, and in fact one of their principal uses is for the production of fine atomic lines for the spectroscopic analysis of small amounts of material. For the examination of molecular spectra, the dimensions of the hollow cathode are usually greater than for this latter type of work.

(iii) *Electric arc and spark*. These two methods have been extensively employed for the production of line spectra of metals and of solid or liquid materials capable of being contained in an electrode. They can be further classified as open or enclosed; in the first case the arc or spark is used in air and in the second it is enclosed in an atmosphere of some gas other than air. The application of these sources to the emission spectroscopy of gases is not greatly developed. Obviously, for this application, the enclosed arc or spark is the only one to be considered. Apart from the fact that the source operates in a tube filled with some gas, the technique is the same as that used for the open source. Because of the negative potential-current characteristics of an arc after striking, it is necessary to incorporate a ballast resistor to achieve stability of operation. The actual methods used to obtain steady arc or spark sources are described in various text-books and will not be described further here.^{5,6}

The enclosed arc or spark may be operated in various gases and at a variety of pressures, from a few mm pressure of Hg up to many atmospheres. As with the other

methods, reduction of the gas pressure favours a greater degree of ionisation. The use of large pressures of gas is sometimes useful in obtaining spectra not otherwise obtainable, such as those of the hydrides of tin and lead.

The great disadvantage of these two techniques, from the standpoint of gas emission spectroscopy, is that the spectra obtained almost always arise from molecules containing the material used in the poles. There are a few cases, however, where this is not so; for instance, if water vapour is present, such arcs or sparks will give the OH band spectrum, and some, particularly the copper arc, will give in air the NO γ bands.

(iv) *Flames*. As with the methods described in section (iii) the use of flames in analytical spectroscopy has so far been mainly concerned with the production of line spectra for metal analysis. In general, the degree of excitation attained in a flame is not as high as in the other methods previously described. This results in the absence of bands from ionised species. The spectra obtained from flames largely arises from unstable radicals produced in the combustion process. Since most flames used in practice employ oxygen as the supporter of combustion, the band spectrum of OH is a very prominent feature. When hydrocarbons are present there is also strong emission from CH, C₂, CO, CO₂ and CH₂O. This results in a rather complex total spectrum, in which it is difficult to identify the bands of other entities. This difficulty, combined with the fact that there is usually very little emission attributable to stable polyatomic molecules, makes the method of very limited application in gas emission spectroscopy.

(b) *Methods of recording spectra*

Spectra may be recorded either photographically or photoelectrically. The photographic method employs a spectrograph, which may be of the prism or grating type, and records the whole of the desired spectral region in one operation, on a photographic plate or film. The exposure time will depend on the brilliance of the source employed, and the wavelength region which is of interest will determine the preferable type of photographic emulsion. The method has intrinsic value in exploratory work, since one can see at a glance the wavelength regions in which emission is occurring. Quantitative work, however, requires the use of plate or film photometry, in which one must relate the extent of blackening of the photographic emulsion with the concentration of the emitting species. Although the technique of photographic photometry has been extensively used in the past and can achieve good results when rigorous precautions are taken,⁶ it is now accepted that it cannot compete in accuracy and ease of execution with modern photoelectric methods. There are many variables to be kept constant in plate or film photometry; for example, the type of emulsion used, the development time, and the processing technique; and this results in the technique being rather cumbersome and subject to errors.

The photoelectric method, entailing the use of a spectrophotometer, which may be of the automatic recording type, is now used widely for quantitative spectrochemical analysis. Such an instrument, instead of giving the whole spectrum in one operation, scans through the wavelength range, the emitted frequencies being allowed to fall in succession on some type of photoelectric detector. The amplified signal from this may be read off from a meter, or may be used to drive a chart recorder, thus giving a direct measure of the intensity of light at each particular wavelength, without any

need for the rather roundabout series of operations required in work using a spectrograph.

The combination of the two techniques offers the most complete and satisfactory method of spectroscopic analysis for gases, the spectrograph being used for initial exploratory work and the spectrophotometer for detailed quantitative analysis.

INVESTIGATIONS AND ANALYTICAL APPLICATIONS OF MOLECULAR EMISSION SPECTRA

(a) *Inert and other permanent gases*

As early as 1922, methods were described for determining the quantity of krypton and xenon in gas mixtures by adding argon as an internal standard.⁷ The actual spectroscopic determination of argon in argon-nitrogen mixtures was described by Leimpt and Visser,⁸ and Frish⁹ developed a method for analysing helium-argon mixtures.

The spectroscope was applied by Gunther and Paneth¹⁰ to the micro-analysis of traces of hydrogen and neon in helium. A year earlier, Klauer¹¹ had given limits of sensitivity for the detection of hydrogen in helium, helium in hydrogen, hydrogen in argon, and argon in hydrogen-gas mixtures. Analytical working curves have been determined for hydrogen, nitrogen, oxygen and carbon monoxide in the presence of excess helium using a small amount of argon as the internal standard.¹²

The spectrographic determination of deuterium present in mixtures with hydrogen, hydrogen sulphide and ammonia has been described by van Tiggelen.¹³

The determination of nitrogen by emission methods has received a great deal of attention. Monfils and Rosen¹⁴ have examined the determination of traces of nitrogen in argon; and Wijnen and van Tiggelen¹⁵ have described the determination of nitrogen and carbon dioxide in mixtures of these gases and in the presence of oxygen. The relative band intensities of the nitrogen molecular ion spectrum were used by Fan¹⁶ to compare the excitation effect of different species of charged particles on a rarefied air sample. A very detailed study of the emission spectrum of air has recently been published.¹⁷ The relative intensities of the spectra from mildly excited discharges in nitrogen, air, nitrous oxide, oxygen and mixtures of these gases have been studied under high resolution as a function of pressure. A study of the emission band spectrum of nitrogen under pressure had previously been reported by Leycuras.¹⁸

The spectroscopic determination of nitrogen in respiratory gases is an important aspect of aviation medicine, and progress in this field has been reviewed by White, Lovelace and Hirsch.¹⁹ Commercial instruments known as Nitrometers have been developed which measure the intensity of the nitrogen system after excitation in a gas discharge tube at reduced pressure. Many modifications of this technique are described and the practical limitations are discussed. Methods are also described for the determination of oxygen and carbon dioxide in respiratory gases.

A simple method for determining nitrogen in argon has been suggested. The total intensity of the emission in a discharge tube containing the mixture is compared with the intensity of the nitrogen bands, which are isolated by means of a filter.²⁰ An alternative approach to the measurement of the purity of inert gases is proposed by Riley²¹ who uses the colour and appearance of discharges in gaseous mixtures as a criterion of the purity.

Preliminary studies on the excitation of the spectra of inorganic gases by high frequency excitation have been reported²² from the authors' laboratory, and quantitative applications are at present under investigation.

Data on the emission molecular spectra of many gases including bromine, carbon monoxide, carbon dioxide, chlorine, fluorine, hydrogen, helium, nitrogen, ammonia, nitrous oxide, oxygen, sulphur monoxide and sulphur dioxide are tabulated in the reference work of Pearse and Gaydon.⁵

(b) *Benzene and benzene derivatives*

Publications devoted to analytical applications of polyatomic emission molecular spectra are almost non-existent. To date, interest has been concentrated on obtaining molecular spectra characteristic of an undissociated molecule, or, where fragmentation has occurred in the process of excitation, on attempts to identify the fragments. The first major investigation of the emission spectra of organic compounds was made by Stewart and co-workers²³ in the 1920's. Nearly one hundred and forty compounds were excited with a form of Tesla discharge, and the compounds which emitted radiations were grouped into five main categories depending on the general appearance of the resultant spectra. In most cases, continuous bands of emission were obtained because of the low dispersing power of the spectrographic equipment used. Attempts by Austin and Black²⁴ to use these spectra to identify the purity of a solvent were not successful, but these authors succeeded in confirming the wavelengths of the benzene bands and in identifying the nature of the side products formed in discharges passed through a number of organic vapours. A spectroscopic study of the decomposition and synthesis of organic compounds by electrical discharges was made a couple of years later, and dissociation of the organic molecule into atomic and ionic fragments was found to be an important factor in the maintenance of the discharge.²⁵

A continuing series of papers by Schuler and co-workers has done much in recent years towards building up an understanding of the source of the spectra. In 1941, pure emission spectra of undecomposed benzene derivatives were obtained by electron collision in the glow discharge.²⁶ In the following year, a further series of benzene derivatives were studied by means of a glow discharge in krypton and hydrogen. In the ultraviolet region, the emission corresponded to the absorption spectrum, but in the visible range additional bands were observed which were ascribed to the dissociation of activated phenyl radicals.²⁷ A later publication demonstrated the similarity of the natural decomposition spectra of benzene derivatives and the spectra resulting from their phospholuminescence in the solid state.²⁸ Direct proof of the existence of short-lived aromatic radicals, based on their emission spectra, was put forward by Schuler and Reinebeck²⁹ in 1949, and the spectrum of the CHO radical was found in the emission spectrum of formaldehyde.³⁰

In 1950 a new type of discharge tube was designed,³¹ and a method of varying the excitation conditions for organic substances was proposed.³² By examining benzene evaporated into a cell containing helium, four new spectra were found.³³ By increasing the naphthalene vapour pressure in a helium discharge a new spectrum besides the helium line and bands of C₂ and CH appeared.³⁴ Five types of compounds, including acetylene, ethylene and aromatic molecules, were subsequently studied to find the groups responsible for the newly found spectra.³⁵ Further work using the mono-derivatives of benzene³⁶ indicated that the common fragments

observed in the glow discharge could possibly be one of four species. Subsequent work by Walker and Barrow³⁷ showed that the simplest interpretation involves the presence of an emitter such as C_6H_5C . These bands were found under excitation conditions intermediate between those giving the spectrum of the complete molecule and those which result in appreciable dissociation into small fragments, *e.g.*, CH. A vibrational analysis of the visible spectrum of the benzyl radical has recently been proposed.³⁸

In 1954, Schuler and Reinebeck³⁹ surveyed the results of emission spectroscopy of organic molecules in the low pressure discharge, and concluded that the spectra obtained did not correspond to transformations between highly excited states of the molecules introduced, but indicated instead the fragmentation of these molecules. In subsequent studies, the excitation conditions were varied and it was shown that the spectra obtained were reproducible if the conditions of discharge were standardised.^{40,41,42} It was suggested that collision between the excited and non-excited initial molecule plays an important part in the phenomenon of luminescence of organic molecules in a glow discharge. Schuler's results on benzene and chlorobenzene have been confirmed by Danilova,⁴³ and confirmation of decomposition and synthesis reactions in the glow discharge has been provided by Nishi and Hamanura.⁴⁴

The emission spectra of benzene, toluene and xylene vapours excited by a high frequency (Tesla type) discharge have also been studied by Agirbiceanu and Hagiiescu.⁴⁵ Solid polymerisation products and continuous emission backgrounds were observed, but none of the spectra suggested the presence of free radicals, fragments or impurities. The benzene spectrum had previously been re-examined by Asundi and Padhye⁴⁶ and the same authors had reported a series of emission bands for toluene.⁴⁷ The emission bands of aniline produced by a variety of excitation methods had also been recorded.⁴⁸ A high frequency electrodeless discharge was used by Robinson⁴⁹ to excite the spectra of benzaldehyde and acetophenone. A later, more complete analysis of the benzaldehyde spectrum has been reported by Garg and Singh⁵⁰ who excited the flowing vapour with an uncondensed transformer discharge. The same type of discharge was used by Upadhyaya⁵¹ to study the emission bands of benzotrifluoride.

Asundi and Joshi have used a high-frequency discharge to obtain emission spectra from benzonitrile⁵² and *p*-dichlorobenzene.⁵³ An ozoniser type of discharge was used to produce an emission spectra from the three isomeric fluorotoluenes.⁵⁴ Spectra for tetrahydronaphthalene⁵⁵ and naphthalene⁵⁶ vapours have recently been reported.

Paillous has made an intensive study of the emission spectra of toluene,⁵⁷ fluorobenzene,⁵⁸ benzonitrile⁵⁹ and aniline.⁶⁰ Over two hundred bands were identified in each case and a vibrational assignment of the frequencies was attempted.

(c) *Miscellaneous organic compounds*

The emission spectrum of formaldehyde was found by Schuler and Reinebeck³⁰ to be identical with the fluorescence spectrum. The same compound was studied by Robinson⁶¹ using a high dispersion spectrograph and a technique originally developed in a study of the spectrum of acetaldehyde.⁶² The rotational structure of the emission bands of formaldehyde has been discussed by Fauris⁶³ and new bands in the emission spectra of acetaldehyde were reported by Régner.⁶⁴

The glow discharge apparatus used previously by Schuler and Reinebeck to study benzene derivatives was also utilised by these workers to study the emission of biacetylene.⁶⁵

The passage of a high-frequency discharge through methane and the vapours of aliphatic alcohols was found to produce the spectra of decomposition fragments.⁶⁶ Spectra attributable to decomposition products were also detected in the emission spectra of CCl_4 and $\text{C}_2\text{F}_2\text{Cl}_2$.⁶⁷

The decomposition of compounds under high frequency excitation was utilised by Keller and Smith⁶⁸ in the development of a spectrographic method for the detection of halogens. Excellent iodine, bromine and chlorine identifications were obtained with organic and inorganic compounds, and the limits of detection were of the order of a fraction of 1%.

Another analytical application of gaseous discharges has been the development of a Tesla discharge detector for gas chromatography.⁶⁹ The discharge of a gas is visibly altered by small amounts of added vapour, and the new detectors measure either the emitted light intensity or the d.c. signal produced by inserting a pair of probe electrodes asymmetrically in the discharge.

DISCUSSION

The general precautions that must be taken to ensure reliable results in the spectrochemical analysis of gases have been listed by Twyman.⁷⁰ Twyman, as would be expected from the previous theoretical discussion, has emphasised that the gas pressure in the tube and the conditions of excitation must be carefully controlled, because the ratio of the line intensities of two components may vary with pressure, even though the two gases are present in the same proportion. Twyman also advises that measures be taken to avoid the effects of a variable concentration of a third constituent, since the presence of a third gas can influence the ratio of the line intensities of two components. Because the rate of "clean up" in the electric discharge varies with the nature of the gas, the apparent proportions of the gases in a sample may change with the time of running of the discharge.

It is further suggested that care must be taken to remove occluded gases from the inside walls of the discharge tube and from the electrodes (if inside the tube) before filling with the sample. Achievement of this ideal often requires prolonged baking of the cell at temperatures up to 450°. The importance of the condition of the cell has been emphasised by Frish,⁹ who has also reviewed the problems associated with the spectrochemical analysis of gases. One of the main difficulties encountered by Frish was the fact that the composition of the gaseous mixture varied during analysis because of adsorption and desorption on the tube walls. Another important problem was that of establishing the optimum conditions for the excitation of the spectrum of the impurities being analysed, since the composition of the mixture had a strong effect on the conditions of discharge.

These difficulties have not prevented the successful analysis of gases by spectroscopic means; and, in fact, the spectroscopic analysis of respiratory gases now appears to have become the accepted technique.¹⁰ Great care must be paid to the standardisation of conditions, but successful extension to the analysis of the rare gases seems highly feasible and experimental work along these lines is now proceeding in our laboratories.

On the other hand, extension of the emission technique to the analysis of organic compounds seems highly improbable. Tesla excitation is said to cause less decomposition of the excited species than alternate modes of excitation, but a constant flow of vapour is considered advisable.⁵ However, decomposition does still occur and at least two attempts^{22,24} have been made to analyse the products deposited on the walls of the glass retaining vessels. In both cases the compounds were concluded to be condensed or polymerised molecules. In a spectroscopic study of the chemical reactions which occur in electrical discharges through organic vapours²⁵ it was found that the simple ionisation of the molecules and the resultant formation of clusters was less important, and the breaking down into molecular and atomic fragments more important than has heretofore been supposed. More recently, Schuler and Stockburger⁴² examined the spectra of a number of substituted benzene derivatives, and found that the excitation caused a splitting off of a small molecule, the remainder being stabilised by double-bond formation, ring-closure or dimerisation. In another study⁷¹ a high-frequency discharge through flowing carbon tetrachloride vapour was found to yield the spectrum of CCl, produce free chlorine, and deposit a small carbonaceous residue.

Apart from complications caused by fragmentation and association of organic compounds during excitation, the complexity of the molecular spectrum produced is in most cases too great for use in analysis.

A final detrimental factor is the ready contamination of the spectra by trace impurities such as air, since these impurities are often preferentially excited. For example, the heating of some organic compounds has been found to release enough air from the sample and the walls of the cell to produce an intense spectrum of nitrogen on excitation.⁷¹ The same detrimental effect was obtained in evacuated cells containing low pressures of gases such as hydrogen, carbon dioxide, chlorine, methane, *etc.*, possibly because of slight leaks of air into the cell.

All forms of emission spectroscopy are renowned for their sensitivity and the characteristic nature of the spectra produced, and these probably constitute the greatest advantages of the technique. In the gaseous phase, if a species is readily excited and gives either a line or simple band spectra, *e.g.*, argon, nitrogen, oxides of carbon, *etc.*, then careful control of conditions permits the development of satisfactory analytical methods. On the other hand if a species is not readily excited, or if the resultant spectrum is fairly complex, emission techniques are far less satisfactory than most other alternate techniques that may be applied to the same problem. Analysis based on the absorption spectrum of a molecule could be a desirable alternative, since there is less tendency for fragmentation or association of excited species; the spectrum is usually comparatively simple; and the interference of impurities on cell walls, *etc.*, is virtually unknown. However, the application of electronic absorption spectra to problems involving the gaseous phase does not appear to have received much attention. The possibilities of this approach will be reviewed in Part II of this series.

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Zusammenfassung—Theoretische und experimentelle Belange der Analyse von Gasen und Dämpfen mittels Emissionsspektroskopie werden diskutiert. Eine Übersicht über die derzeitige Literatur über Molekularemmissionsspektroskopie wird gegeben.

Résumé—Les auteurs ont examiné les aspects théoriques et expérimentaux de l'analyse des gaz et des vapeurs par spectroscopie d'émission et ont passé en revue la littérature courante sur la spectroscopie d'émission moléculaire.

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SHORT COMMUNICATION

The use of vanadium^V-sulphosalicylic acid complex as a redox indicator

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In a previous communication¹ it was reported that vanadium^V gives an intense turquoise-blue colour with sulphosalicylic acid in concentrated sulphuric acid and that the colour reaction is specific and very sensitive for the detection of vanadium^V. During our studies on the nature of the complex, it was found that vanadium^{IV} gives a negative colour test and that the blue colour developed by the reagent with vanadium^V is discharged on the addition of a reducing agent like iron^{II}, uranium^{IV} or hydroquinone. It was also observed that the blue colour is restored by the addition of cerium^{IV} solution. This reversible property of the complex has been further investigated to see if the complex can be used as a redox indicator.

EXPERIMENTAL

Our experiments have shown that

- (a) sulphosalicylic acid undergoes oxidation by potassium permanganate or cerium^{IV} sulphate in a sulphuric acid medium, but phosphoric acid prevents the oxidation of sulphosalicylic acid by cerium^{IV} sulphate although not by potassium permanganate,
 - (b) there is no appreciable reaction between sulphosalicylic acid and potassium dichromate within the time required for a titration,
- and (c) the complex dissociates at higher temperatures.

In view of these observations, it may be concluded that a small amount of vanadium^V-sulphosalicylic acid complex may be used as an internal indicator in the titration of iron^{II} with potassium dichromate in 20*N* sulphuric acid (an acidity required to give a sufficiently intense blue colour when vanadium^V and sulphosalicylic acid are mixed) and with cerium^{IV} sulphate in 20*N* sulphuric acid in the presence of phosphoric acid. It is also evident that it cannot be used as an indicator for titrations with potassium permanganate because it discharges the colour of the complex by oxidising the sulphosalicylic acid ligand.

Indicator solution

This is prepared by dissolving 0.12 g of ammonium vanadate and 2 g of sulphosalicylic acid in 100 ml of concentrated sulphuric acid. A volume of 0.2 ml of this solution is found to be sufficient for 50 ml of titration mixture. It is not necessary to prepare this solution beforehand, because the complex can be produced *in situ* by adding the requisite quantities of ammonium vanadate and sulphosalicylic acid solutions separately to the titration mixture.

Recommended titration procedure

An aliquot of iron^{II} sulphate solution is taken and sufficient water and concentrated sulphuric acid are added to make up the volume to 50 ml and to keep the acidity at 20*N* at the end of the titration. The solution is cooled to room temperature and 0.2 ml of the indicator solution is added. This solution is titrated, cooling it whenever necessary, with potassium dichromate or with cerium^{IV} sulphate solution after adding 5 ml of 80% phosphoric acid. The end-point is indicated by the solution changing its colour to greenish-blue on the addition of an excess drop of the oxidant. In titrations with potassium dichromate the titration mixture, if necessary, can be diluted with 20*N* sulphuric acid to prevent the green chromium^{III} sulphate interfering with the detection of the end-point. The titres are found to agree with the values obtained from potentiometric titrations carried out at the same acidity.

Redox potential of indicator

The transition potential of the vanadium^V-sulphosalicylic acid complex as an indicator in the titration of iron^{II} sulphate solution with cerium^{IV} sulphate solution in 20*N* sulphuric acid was determined according to the procedure of Belcher, Nutten and Stephen,² and found to be 950 ± 5 mV (N.H.E.).

Acknowledgement—The authors wish to thank Professor G. Gopala Rao for his interest in the work.

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V. PANDU RANGA RAO
D. SATYANARAYANA

Summary—In a previous communication it was reported that vanadium^V gives an intense turquoise-blue colour with sulphosalicylic acid in concentrated sulphuric acid and that the colour reaction is specific and very sensitive for the detection of vanadium^V. During our studies on the nature of the complex, it was found that vanadium^{IV} gives a negative colour test and that the blue colour developed by the reagent with vanadium^V is discharged on the addition of a reducing agent like iron^{II}, uranium^{IV} or hydroquinone. It was also observed that the blue colour is restored by the addition of cerium^{IV} solution. This reversible property of the complex has been further investigated to see if the complex can be used as a redox indicator.

Zusammenfassung—In einer früheren Mitteilung wurde über einen tiefblauen Komplex von Vanadin(V) mit Sulfosalizylsäure in konzentrierter Schwefelsäure berichtet. Die Färbung ist spezifisch für Vanadin(V) und die Reaktion ist sehr empfindlich. Während weiterer Untersuchungen wurde gefunden, dass Vanadin(IV) diese Reaktion nicht gibt. Die Färbung des Vanadin(V) Komplexes wird durch Reduktionsmittel wie Eisen(II), Uran(IV) oder Hydrochinon ausgebleicht, erscheint jedoch auf Zusatz von Cer(IV) wieder. Die Reversibilität der Reaktion wurde untersucht um zu sehen, ob der Komplex als Redoxindikator Verwendung finden kann.

Résumé—Dans une communication précédente, nous avons indiqué que la vanadium(V) donne une coloration bleu turquoise intense avec l'acide sulfosalicylique dans l'acide sulfurique concentré et que cette réaction colorée est spécifique et très sensible pour déceler le vanadium(V). Pendant notre étude sur la nature du complexe, nous avons trouvé que le vanadium(IV) ne donne pas cette réaction et que la couleur bleue obtenue avec le vanadium(V) est déchargée par addition d'un agent réducteur comme le fer(II), l'uranium(IV) ou l'hydroquinone. Nous avons alors observé que la couleur bleue réapparaît par addition d'une solution de cérium(IV). Cette propriété réversible du complexe a été étudiée ultérieurement pour voir si le complexe peut être utilisé comme indicateur rédox.

REFERENCES

- ¹ V. Pandu Ranga Rao and D. Satyanarayana, *Talanta*, 1961, **8**, 846.
- ² R. Belcher, A. J. Nutten and W. I. Stephen, *J. Chem. Soc.*, 1952, 3857.

NOTICES

Material for this section should be sent directly to the Assistant Editor

ARGENTINA

Sunday-Saturday 16-22 September 1962: Eighth Latin-American Congress of Chemistry, on the occasion of the Fiftieth Anniversary of Asociación Química Argentina. Buenos Aires.

The congress is open to chemists from all countries and will be divided into the following sections:

1. Inorganic and Radio-Chemistry
2. Physical Chemistry
3. Organic Chemistry
4. Biological Chemistry
5. Analytical Chemistry
6. Food Chemistry
7. (a) Pharmaceutical Chemistry
(b) Pharmaceutical Industries
8. (a) Industrial Chemistry
(b) Chemical Engineering
9. History of Chemistry and Chemical Education.

Further information can be obtained from the Secretary, Octavo Congreso Latinamericano de Química, Casilla de Correo 2153, Buenos Aires, Argentina.

CANADA

Sunday-Friday 19-24 August 1962: VIII International Congress for Microbiology: Canadian Society of Microbiologists and Canadian Committee on Culture Collections of Micro-organisms under the auspices of the International Association of Microbiological Societies. Queen Elizabeth Hotel, Montreal.

Three symposia or panel discussions will be held each morning and formal invitations have been issued to the speakers. Concurrent paper-reading sessions will normally be held each afternoon.

The following programme has been arranged for the panel discussion on **Automation and Control of Process Variables in Industrial Microbiology**:

J. J. H. HASTINGS (London, England)

Application of Automation to Processes, Analysis, Assay, and Computation. Measurement and Control of Physical Variables.

H. M. SHER (London, England)

Discussant—H. J. HROCH

J. F. PAGANO (New Brunswick, U.S.A.)

Automatic Devices for Microbiological Assay of Antibiotics.

Discussant—J. M. KELLY

V. L. SINGLETON (Davis, U.S.A.)

Applications of Liquid Chromatographic Techniques to the Production and Analysis of High Quality Products.

Discussant—J. R. GERKE

A. FERRARI (Chauncey, U.S.A.)

Application of Methodology of Chemical and Biochemical Analysis with an Autoanalyzer Instrumental System.

Discussants—G. E. REINHARDT, G. E. SCHAIBERGER

J. A. KEARNS (New York, U.S.A.)

The Electronic Computer in Microbiological Control.

Discussant—G. E. BOND

Further information can be obtained from the Secretariat, VIII International Congress for Microbiology, 3574 University Street Montreal, Canada.

FRANCE

La 5ème réunion de la Commission Internationale d'Analyses (CIA) du Comité International de la Detergence (CID) s'est déroulée à Paris, les Lundi 9 et Mardi 10 Octobre 1961, sous le présidence du Professeur JACINI (Italie).

Huit pays participaient à cette réunion: Allemagne, Belgique, Espagne, France, Grèce, Italie, Pays-Bas, Suisse. On remarquait aussi la présence d'un délégué de l'Association Internationale de la Savonnerie et de la Detergence (AIS), qui est membre consultatif du CID, et d'un observateur de l'Organisation Internationale de Normalisation (ISO).

Au cours de l'année 1960/1961, différentes analyses circulaires ont été effectuées dans les pays membres de CIA en suivant les méthodes d'analyses en examen au sein de cette Commission et en utilisant des produits définis fournis par des laboratoires désignés à cette fin. Les résultats de ces analyses se sont révélés concordants. Après discussion des résultats obtenus et certaines modifications suggérées en séance, les méthodes d'analyses des *alkylsulfonates de sodium* et *alkylsulfates primaires de sodium* pourront bientôt être considérées comme suffisamment précises pour être soumises à l'ISO aux fins d'homologation internationale. Auparavant, ces méthodes seront comparées au sein des Commissions nationales avec celles qui seront basées sur l'emploi des résines échangeuses d'ions.

Deux autres méthodes, moins avancées, seront étudiées par analyses-circulaires en 1961/1962; la séparation des alkylsulfates d'une part, et des alkylsulfonates de l'autre, des *non-ionique*. En ce qui concerne ces derniers produits, il a été jugé bon de réunir prochainement certains membres de CIA à Bruxelles, pour une "journée d'information non-ionique".

Quant aux *savons purs*, les méthodes d'analyses adoptées sont celles de l'Union Internationale de Chimie Pure et Appliquée (IUPAC). Par ailleurs, et en accord avec cet organisme, quatre méthodes supplémentaires figurent au programme de travail de CIA dont deux (dosage du glycérol, détermination de l'insaponifié) seront bientôt circularisées aux membres de la Commission.

Il a été ensuite décidé que la prochaine session de la CIA se tiendrait à Bruxelles, sur invitation du Comité Belge de la Detergence, en Septembre, 1962. Le délégué grec a par ailleurs invité ses collègues à se réunir à Athènes en 1963.

POLAND

Among the 225 participants at the **Third Polish Spectral Emission Conference** in September, 1961 (see also *Talanta*, 1961, **8**, 174), there were 63 from Hungary, 21 from German Democratic Republic, 10 from Czechoslovakia, 3 from France, and 1 each from Russia, Italy, Yugoslavia and Bulgaria.

In the scientific programme 54 short communications were announced, covering all fields of emission spectroanalysis. The majority of the communications dealt with the analysis of non-conductive samples (18), the analysis of solutions (14) and general problems (13). The Organisation Committee invited 6 scientists to deliver plenary lectures on the most important topics in emission spectroscopy: Dr J. ŚWIETOSŁAWSKA (Poland), The Addition Method in Emission Spectral Analysis; Dr. T. TÖRÖK (Hungary), Actual Possibilities and Problems of the Quantitative Evaluation of Spectra on Photographic Plates; Dr. H. MORITZ (German Democratic Republic), The World Development of Spectral Analysis; Ing. M. MATHERNY (Czechoslovakia), The Emission Spectrochemistry of Solutions; Professor A. K. RUSANOV (Russia), Particular Features of the Spectral Analysis of Powder Materials; Dr. J. CZAKOW (Poland), The Quantitative Spectral Analysis of Traces.

UNITED KINGDOM

Wednesday 10 January 1962: Symposium on Developments in Gas Chromatography as Applied to Polymers: Mr. D. H. DESTY, Dr. C. A. FINCH and Dr. R. S. LEHRLE: *Society for Analytical Chemistry, Midlands Section*. The University, Edgbaston, Birmingham, 15. 2.30 p.m.

Wednesday 10 January 1962: Precision Balances—History, Development and Techniques: Mr. A. O. BROOKS: *Aberdeen and North of Scotland Sections of Chemical Society, Royal Institute of Chemistry and Society for Chemical Industry*. Chemistry Department, University, Old Aberdeen.

Friday 12 January 1962: Annual General Meeting followed by Radioactivity Measurements in Monmouthshire: Dr. G. V. JAMES: *Society for Analytical Chemistry, Western Section*. University College, Cardiff.

Tuesday 16 January 1962: Some Aspects of the Work of a Public Analyst: Mr. R. W. SUTTON: *Royal Institute of Chemistry, East Midlands Section*. Derby and District College of Technology, Kedleston Road, Derby. 7.30 p.m.

Wednesday 17 January 1962: Complexometric Titrations: Professor H. M. N. H. IRVING: *Royal Institute of Chemistry, North Wales Section*. Flintshire Technical College, Connah's Quay, Nr. Chester.

Wednesday 24 January 1962: Discussion Meeting: *Society for Analytical Chemistry, Microchemistry Group*. The Feathers, Tudor Street, London, E.C.4. 6.30 p.m.

Friday 26 January 1962: Annual General Meeting followed by Application of Analysis to Research Problems in the Gas Industry: Mr. G. R. BOREHAM: *Society for Analytical Chemistry, Scottish Section*. Grosvenor Restaurant, Gordon Street, Glasgow. 1.30 p.m.

Saturday 27 January 1962: Annual General Meeting followed by The Work of the Laboratory of the Government Chemist: Dr. D. T. LEWIS: *Society for Analytical Chemistry, North of England Section*. City Laboratories, Mount Pleasant, Liverpool. 2.15 p.m.

Monday-Friday 9-13 April 1962: Feigl Anniversary Symposium: *Society for Analytical Chemistry, Midlands Section*, under the patronage of I.U.P.A.C. University, Edgbaston, Birmingham, 15 (see also *Talanta*, 1961, 8, 561 and 765).

Plenary lectures will be given by:

Professor Dr. Ing. F. FEIGL (Ministry of Agriculture, Rio de Janeiro, Brazil)

Professor R. BELCHER (University of Birmingham, U.K.) and Professor P. W. WEST (Louisiana State University, U.S.A.)

Professor F. WELCHER (University of Indiana, U.S.A.)

Professor H. MALISSA (Technical University, Vienna, Austria)

The Development of Spot Test Analysis and the Chemistry of Specific, Selective and Sensitive Reactions.

An Appreciation of the Contribution of Fritz Feigl to the Development of Analytical Chemistry.

The Development of Organic Reagents for Inorganic Analysis.

From Spot-Tests to Spot-Colorimetry.

The detailed scientific programme, subject to additions and minor alterations, is as follows:

D. M. W. ANDERSON (University of Edinburgh, U.K.)

C. V. BANKS (Iowa State University, U.S.A.)

E. BERG (Louisiana State University, U.S.A.)

J. BERGER (Danish School of Pharmacy, Denmark)

E. BISHOP (University of Exeter, U.K.)

T. BURKHALTER (Texas Instruments Inc., U.S.A.)

J. K. CARLTON (Louisiana State University, U.S.A.)

R. A. CHALMERS (University of Aberdeen, U.K.)

F. CLANET (C.E.A., Radiochemical Laboratory, France).

D. COOKE (Cornell University, U.S.A.)

T. A. DAVIES [International Nickel Co. (Mond) Ltd., Birmingham, U.K.]

C. DUVAL (C.N.R.S. Research Laboratory, France)

G. V. M. DUYNCKAERTS (University of Liege, Belgium)

P. J. ELVING (University of Michigan, U.S.A.)

W. T. ELWELL (I.C.I. Ltd., Metals Division, Birmingham, U.K.)

Analytical Applications of Infrared Spectroscopy.

Vicinal Dioximes as Analytical Reagents.

Separation of Some Transition Metals by Counter-Current Extraction.

Derivatives suitable for Identification of Organic Acids.

Differential Electrolytic Potentiometry.

Chromatographic Determination of Trace Elements in Capacitor Grade Tantalum.

Streak Reagents for Colourless Zones in Adsorption Chromatography.

Redox Potentials and Qualitative Analysis.

Spot-Testing for Transuranic Elements.

Atomic Absorption Spectroscopy with Continuous Sources.

Application of Solids Mass Spectroscopy to Metallurgical Analysis.

The Existence of the Uranyl Ion.

Extraction of Phosphate Esters.

Microanalysis with the Graphite Indicating Electrode.

Atomic Absorption Spectroscopy.

- L. ERDEY (Technical University, Budapest, Hungary)
- H. FREISER (University of Arizona, U.S.A.)
- D. GIBBONS (A.E.R.E., Harwell, U.K.)
- D. GOLDSTEIN (Ministry of Agriculture and Mineral Products, Brazil)
- L. GORDON (Case Institute of Technology, U.S.A.)
- J. B. HEADRIDGE (University of Sheffield, U.K.)
- H. M. N. H. IRVING (University of Leeds, U.K.)
- W. KEMULA (University of Warsaw, Poland)
- I. M. KOLTHOFF (University of Minnesota, U.S.A.)
- G. KORTUM (University of Tubinger, Germany)
- H. A. LAITINEN (University of Illinois, U.S.A.)
- D. T. LEWIS (Laboratory of the Government Chemist, London, U.K.)
- R. J. MAGEE (Queen's University, Belfast, U.K.)
- G. MATTOCK (Electronic Instruments Ltd., Richmond, U.K.)
- A. C. MENZIES (Hilger & Watts Ltd., U.K.)
- G. W. C. MILNER (A.E.R.E., Harwell, U.K.)
- F. L. MOORE (Oak Ridge National Laboratory, U.S.A.)
- G. H. MORRISON (Cornell University, U.S.A.)
- L. J. OTTENDORFER (Technical University, Vienna, Austria)
- F. H. POLLARD (University of Bristol, U.K.)
- R. PŘIBIL (Academy of Sciences, Prague, Czechoslovakia)
- R. C. ROONEY (Southern Analytical Ltd., Camberley, U.K.)
- E. SAWICKI (Health Dept., Cincinnati, U.S.A.)
- P. SENISE (University of Sao Paulo, Brazil)
- E. SCHULEK (L. Eötvös University, Budapest, Hungary)
- A. A. SMALES (A.E.R.E., Harwell, U.K.)
- G. F. SMITH (University of Illinois, U.S.A.)
- H. SPECKER (Dortmund Institute of Spectroscopy, Germany)
- W. I. STEPHEN (University of Birmingham, U.K.)
- H. SUTER (Celanese Chemical Co., Clarkwood, Texas, U.S.A.)
- S. VIEBEL (Polytechnic Institute, Copenhagen, Denmark)
- Standard Sulphur Solutions for the Non-Aqueous Titration of Cyanide and Selenium. Use of Organic Reagents in Solvent Extraction.*
- Computer Coupled Automatic Activation Analysis.*
- A New Spot-Test for Sulphur in Organic and Inorganic Compounds.*
- Precipitation Processes.*
- Analytical Application of Redox Reactions in Hydrofluoric Acid.*
- (to be announced)
- Chromato-polarography.*
- Induced Reactions.*
- Diffuse Reflectance Spectroscopy in Analytical Chemistry.*
- Molybdenum Catalysed Reduction of Perchlorate.*
- The Use of Bismuth Radionuclides in Analysis.*
- Spectrophotometric Determination of Niobium in presence of Tantalum and Associated Elements.*
- The Analytical Applications of Alkali Cation-Sensitive Electrodes.*
- Aspects of Atomic Absorption Spectroscopy.*
- Electrochemical Analysis in Atomic Energy.*
- High Molecular Weight Amines—Versatile Extractants.*
- Extension of Sensitivity in Trace Element Analysis.*
- Chronoautoradiographic Estimation of Small Amounts of Radioactive Materials.*
- New Reagents Specially designed for Chromatographic Use.*
- New Rapid Methods for Alloy Analysis.*
- Recent Developments in Cathode Ray Polarography.*
- Spot-Test Detection and Spectrophotometric Determination of Formic Acid.*
- Aspects of Extractability of Phosponium Salts and Related Compounds.*
- Determination of Small Amounts of Carbon Dioxide from Decarboxylation of Organic Compounds.*
- Recent Analytical Work using Specific and Sensitive Nuclear Methods.*
- Deuterium Perchlorate.*
- Trace Analysis by "Inverse Polarography".*
- Reagents for the Nitrate Ion.*
- (to be arranged)
- Detection, Characterisation and Estimation of Carboxylic Acids and Esters.*

- A. WALSH (C.S.I.R.O., Melbourne, Australia)
 H. F. WALTON (University of Colorado, U.S.A.)
- H. WEISZ (University of Freiburg-Breisgau, Germany)
 P. W. WEST (Louisiana State University, U.S.A.)
 A. F. WILLIAMS (I.C.I. Ltd., Nobel, Division, Stevenston, U.K.)
 C. L. WILSON (Queen's University, Belfast, U.K.)
- H. N. WILSON (I.C.I. Ltd., Billingham Division, U.K.)
 P. ZUMAN (C.S.A.V. Polarography Institute, Prague, Czechoslovakia)
 J. ZYKA (Charles University, Prague, Czechoslovakia)
- Atomic Absorption Spectroscopy in Australia.*
New Ion-Exchange Methods for Analytical Separation.
Semi-quantitative Analysis by Spot Reactions: A Review of New Reactions.
 (to be announced)
Quantitative Aspects of Gas Chromatography and the Analysis of Blasting Explosives.
Separation and Identification of Some Anions on the Microgram Scale.
X-ray Fluorescence.
- Polarography in Functional Analysis.*
New Oxidation-Reduction Titrations.

Sunday-Saturday 9-15 September 1962: Fifth Triennial Summer School in Analytical Chemistry: Royal Institute of Chemistry with the participation of Society for Analytical Chemistry. Manchester College of Science and Technology.

The School will consist of four separate, but concurrent, courses:

Course I—*Physical Methods of Organic Chemistry*

Course Leader: Dr. D. W. MATHIESON, Reader in Pharmaceutical Chemistry, School of Pharmacy, London, W.C.1.

Course II—*Recent Developments in Inorganic Analysis*

Course Leader: Mr. W. T. ELWELL, Chief Analyst, I.C.I. Ltd., Metals Division, Witton, Birmingham, 6.

Course III—*Determination of Toxic Substances in the Air and Effluents*

Course Leader: Mr. H. E. STAGG, Chief Analyst, I.C.I. Ltd., Dyestuffs Division, Blackley Manchester.

Course IV—*Newer Instrumental Techniques*

Course Leader: Dr. V. S. GRIFFITHS, Reader in Spectroscopy, Battersea College of Technology, London.

Further information may be obtained from Mr. D. G. CHISMAN, Education Officer, Royal Institute of Chemistry, 30, Russell Square, London, W.C.1.

The Fourth Edition (1961) of the **Directory of Independent Consultants**, compiled by the Royal Institute of Chemistry, is now available and can be supplied gratis to bona fide enquirers for consulting services in chemistry and related subjects. It covers a wide range of consultant services offered by 156 independent practices in Great Britain and Ireland, operated and controlled by Fellows or Associates of the Royal Institute of Chemistry, which are not part of any other organisation.

The general plan of the directory is similar to that adopted in other editions, but the basis of the subject guide has been revised to take account of the number and variety of fields of specialisation, and to make it easier to refer to the main section of the directory in finding consultants most likely to help in a particular field.

Further lists of books received from U.S.S.R. and translated books were issued by the National Lending Library for Science and Technology of D.S.I.R. in October and November 1961 (see also *Talanta*, 1961, 8, 690). To simplify and accelerate the compilation of the list, an English translation of each Russian title has now been omitted.

Literature available in the National Lending Library may be consulted in the reading room at Boston Spa, Yorkshire, between the hours of 9 a.m. and 5 p.m. on Mondays to Fridays excluding official holidays.

Publications listed by the Library may be borrowed by sending Science Museum Library loan requisition forms direct to Boston Spa. Organisations which at present do not borrow from the Science Museum Library, but wish to borrow literature from the National Lending Library, should write to the Keeper of the Science Museum Library, London, S.W.7, and ask to be considered for the Science Museum Library's list of approved borrowers. When approved in this way, loan requisition forms will be provided.

The following New British Standards are announced in *B.S.I. News: B. S. 1728: Methods for the analysis of aluminium and aluminium alloys: Part 12: 1961: Silicon*. This specifies reagents required, recommended methods of sampling, and analytical procedure for the determination of silicon in alloys having a silicon content of between 0.02 and 0.3%. (Price 3s.)

B.S. 3422: 1961: Laboratory deflection pH meters. This specifies essential performance requirements for laboratory deflection pH meters intended primarily for general laboratory use, and includes portable and battery operated instruments; it covers single pH scale and multi pH scale types. (Price 4s.)

Also announced are the following Revised British Standards:

B.S. 1121: Methods for the analysis of iron and steel: Part 20: 1961: Tin in iron and steel. This describes a method applicable to iron and steel containing up to 0.25% of tin. (Price 2s.6d.)

Part 37: 1961: Nickel in iron and steel and permanent magnet alloys. This describes two methods applicable to iron and steel and permanent magnet alloys. Method A covers the range of nickel contents in iron, steel, and permanent magnets of the aluminium-nickel-cobalt type, provided that the cobalt in the test solution does not exceed 0.15 g. Method B is intended for cobalt steels containing up to 0.25% of nickel, where the amount of cobalt in the test solution exceeds 0.15 g (Price 4s.) This method supersedes *B.S. 1121: Part 2*, which is now withdrawn.

B.S. 2058: 1961: Lunge-Rey weighing pipette. This specifies the material, construction, essential dimensions and inscriptions for the Lunge-Rey weighing pipette. (Price 4s.)

The following Amendment Slip is announced:

B.S. 1061: Methods for the analysis and testing of coal and coke: Part 5: 1957: Gross calorific value of coal, and coke. Amendment No. 2: PD 4309.

UNITED STATES OF AMERICA

Tuesday 9 January–Thursday 1 February 1962: Fifteenth Annual Symposium on Modern Methods of Analytical Chemistry. Louisiana State University, Baton Rouge, La.

Thursday–Friday 25–26 January 1962: Analytical Division of Fourth Delaware Valley Regional Meeting. Sheraton Hotel, Philadelphia. Two symposia are planned, one on the first day on Separation Techniques, and one on the second day on Laboratory Automation.

Monday 30 April–Thursday 3 May 1962: Thirteenth Annual Mid-American Spectroscopy Symposium: Society for Applied Spectroscopy, Chicago Section in co-operation with Cleveland, Detroit, Indianapolis and St. Louis Sections. Conrad Hilton Hotel, Chicago.

Original papers on the most recent advances in infrared, Raman, optical emission, X-ray, general absorption, nuclear magnetic resonance, electron spin resonance and atomic absorption will be presented. For the first time sessions on vacuum ultraviolet, gas chromatographic preparation of samples for spectroscopic analysis and a nuclear magnetic resonance workshop will be introduced. The popular introductory clinic in infrared spectroscopy will be continued, and problem clinics, seminars and an exhibit featuring the very latest instruments and equipment will be of special interest.

For further information write to Dr. JOHN R. FERRARO, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, U.S.A.

Monday–Friday 18–22 June 1962: International Conference on Spectroscopy, also designated Xth Colloquium Spectroscopicum Internationale: Society for Applied Spectroscopy. University of Maryland College Park, Md., near Washington, D.C.

The purpose of the conference is to promote the exchange of knowledge on current research in important areas of spectroscopy, both basic and applied. The invited lecturers include:

H. KAISER (Dortmund, Germany)

Critical Review of the Methods and Results of Time Resolved Spectroscopy.

C. T. J. ALKEMADE (Utrecht, Netherlands)

Excitation and Related Phenomena in Flames.

A. WALSH (Melborne, Australia)

Atomic Absorption Spectroscopy.

J. L. GREENSTEIN (Pasadena, U.S.A.)

The Role of Spectroscopy in Astrophysics.

T. A. CHUBB (Washington, U.S.A.)

Measurement of Ultraviolet and X-ray Radiation from above the Atmosphere.

L. BELLAMY (Essex, England)

Factors Influencing the Position of Group Frequencies in Infrared Spectra.

H. H. GUNTARD (Zurich, Switzerland)

(to be announced)

J. H. JAFFE (Rehovoth, Israel)

Spectral Line Shape and Molecular Interaction

R. N. JONES (Ottawa, Canada)

Comparative Studies of Infrared and Raman Group Frequencies and their Applications.

A. J. AHEARN (Murray Hill, U.S.A.)

Vacuum Spark Mass Spectrographic Analysis of Solids.

J. BEYNON (Manchester, England)

Correlation of Mass Spectra with Molecular Structure.

C. HUTCHINSON (Chicago, U.S.A.)

Electron Spin Resonance.

R. RICHARDS (Oxford, England)

Applications of Nuclear Magnetic Resonance.

D. H. WHIFFEN (Teddington, England)

Electron Spin Resonance and Free Radical Structure.

B. VODAR (Bellevue)

Extreme Ultraviolet Spectra.

D. A. RAMSAY (Ottawa, Canada)

Spectra of Gaseous Free Radicals.

B. P. STOICHEFF (Ottawa, Canada)

On the Application of Optical Masers to Spectroscopic Studies.

J. PHILIBERT (St. Germain-en-Laye, France)

(to be announced)

V. B. COSSLETT (Cambridge, England)

(to be announced)

In addition to the invited speakers, papers may be submitted on the following spectroscopic subjects: atomic emission and absorption, astrophysical, infrared, Raman and microwave, mass spectrometry, nuclear magnetic resonance and electron spin paramagnetic resonance, ultraviolet and visible, X-ray emission and absorption, education.

Those desiring to present papers should submit titles and abstracts of 250–300 words, before 31 December, 1961, to BOURDON F. SCRIBER, General Chairman, International Conference on Spectroscopy, National Bureau of Standards, Washington 25, D.C., U.S.A.

PAPERS RECEIVED

- A phosphorus pentoxide dessicant employing exfoliated vermiculite as carrier:** G. FREDERICK SMITH and HARVEY DIEHL. (6 October 1961).
- The determination of traces of ruthenium in samples of platinum by neutron-activation analysis:** R. A. KILLICK and D. F. C. MORRIS. (6 October 1961).
- The electrolytic oxidation of oxalate ion in the determination of calcium and magnesium:** JOHN MARTIN and WALTER WAGNER. (7 October 1961).
- Oxidimetric determination of organic compounds by means of strong oxidising agents—A review:** G. DEN BOEF and H. L. POLAK. (13 October 1961).
- Photometric titrations:** J. P. PHILLIPS and ROSE C. COWLEY. (20 October 1961).
- Determination of alkyl cellulose ethers by gas chromatography:** JOHN G. COBLER, E. PAUL SAMSEL and GARTH H. BEAVER. (20 October 1961).
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ERRATA

- Page 228, authors of paper: for Ružička read Růžička.
 Page 492, title of paper: for 1-dithiocarboxy-3-methyl-5-phenyl-pyrazoline read 1-dithiocarboxy-3-methyl-5-phenyl-pyrazole.
 Page 633, line 20: for $k = M\alpha^{-1}k_{MF}$ read $k = \eta\alpha^{-1}k_{MF}$.
 Page 640, reference 120: J. Lustěnc, J. Krekule u. V. Pokorná, *Biol. Plant. (Praha)*, 1960, 2, 223.
 Page 713, caption to Fig. 3: for Silver-Bromopyrogallol colour red system read Silver-Bromopyrogallol red colour system.
 Page 824, title of paper: for Oxidation of cobalt^{III} with iron^{II} chloride in 2,2'-bipyridyl read Oxidation of cobalt^{II} with iron^{III} chloride in 2,2'-bipyridyl solutions.
 Page 898, line 15: for The excitation process in the positive column the collisions of electrons with gas molecules read The excitation process in the positive column results from the collisions of gas molecules.

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¹ J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, 57, 661.

² S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

³ A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.

⁴ W. Jones, *Brit. Pat.* 654321, 1959.

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