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ETUDE POLAROGRAPHIQUE ET PHYSICOCHIMIQUE DE *N*-OXYDES—I

MECANISME DE LA REDUCTION ET HYDRATATION DES FORMYLPYRIDINES *N*-OXYDES

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(*Reçu le* 2 *juillet* 1968. *Accepté le* 12 *août* 1968)

Résumé—Les formylpyridine-2 et -4 *N*-oxydes présentent en milieu acide un mécanisme de réduction anormal: une première vague, située aux potentiels de réduction habituels de la fonction aldéhyde, correspond à la réduction simultanée des fonctions *N*-oxyde et carbonyle; une deuxième vague correspond à la réduction de la fonction *N*-oxyde sous l'influence du substituant hydrate d'aldéhyde. La réduction du formylpyridine-3 *N*-oxyde a lieu normalement à tous les pH (réduction successive des fonctions carbonyle et *N*-oxyde). Les mécanismes de réduction ont été vérifiés par électrolyse à potentiel contrôlé. Les phénomènes d'hydratation du carbonyle ont été étudiés à partir des résultats polarographiques et par spectrophotométrie U.V.

BIEN que de nombreux *N*-oxydes substitués de la pyridine aient déjà été examinés polarographiquement,[1,2] les formylpyridines *N*-oxydes n'avaient fait jusqu'ici l'objet d'aucun travail. Les formylpyridines simples présentent des anomalies dues à l'hydratation du carbonyle, et étudiées en détail par l'un de nous;[3] on pouvait donc s'attendre à retrouver un phénomène du même type pour les *N*-oxydes correspondants.

Les résultats de cette étude nous ont permis de montrer que les formylpyridines *N*-oxydes sont en effet hydratés; d'autre part nous avons pu mettre en évidence un mécanisme de réduction tout à fait anormal pour de tels dérivés.

DESCRIPTION DES POLAROGRAMMES ET EVOLUTION AVEC LE pH

Les polarogrammes se composent de deux types de vagues distinctes. La première vague A, dont la hauteur dépend essentiellement du pH (Fig. 1 à 6), se dédouble pour $pH > 11$ environ en deux vagues A_1 et A_2. La hauteur de A_1 diminue lorsque le pH croît, jusqu'à ce que la hauteur des deux vagues soit égale en milieu très alcalin. Pour le formylpyridine-4 *N*-oxyde, la vague A est également scindée en deux vagues A_1' et A_2' de pH 2 à 10. Pour le formylpyridine-3 *N*-oxyde, la hauteur de la vague A en milieu très acide (acide perchlorique) correspond à une réduction à 2*F*. Pour les formylpyridine-2 et -4 *N*-oxydes, la hauteur de la vague A en milieu acide est bien supérieure: pour le dérivé 4 elle correspond à une réduction à 4*F*.

La deuxième vague B disparaît dans tous les cas vers pH 9 ou 10. Pour le dérivé 3, la hauteur de cette vague correspond à une réduction à 2*F*, sauf vers pH 0. Pour le dérivé 2 et surtout pour le dérivé 4, sa hauteur est beaucoup plus faible.

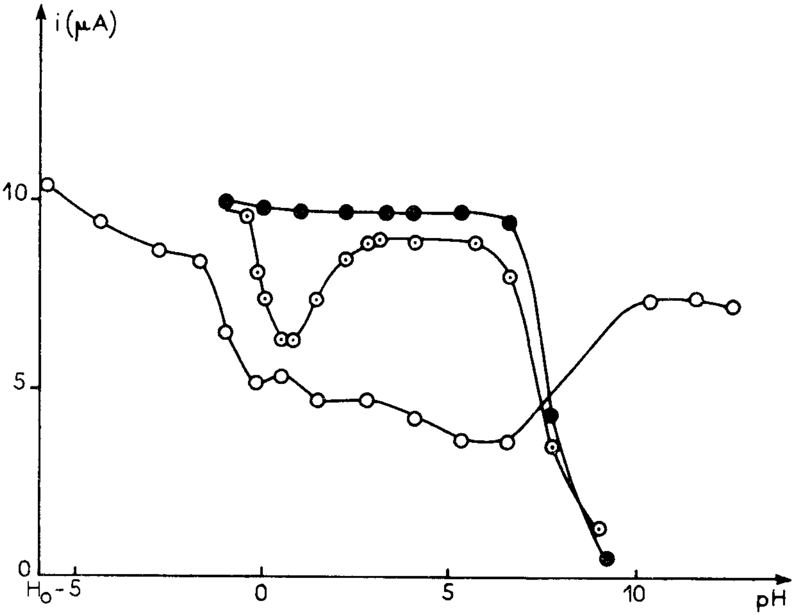


FIG. 1.—Variation du courant limite en fonction du pH.
Formyl-3 pyridine *N*-oxyde: ○, vague A, ou somme des vagues A_1 et A_2; ⊙, vague B.
Hydroxyméthyl-3 pyridine *N*-oxyde: ●.

Il est clair que l'hydratation joue, comme pour les pyridinaldéhydes, un rôle important, et est responsable des variations du courant limite de la vague A en fonction du pH.

La première vague A est certainement liée, d'après son potentiel de demi-vague, à la réduction du carbonyle. A un pH donné son potentiel de demi-vague est voisin de celui des pyridinaldéhydes correspondants[3] (voir Figs. 4, 5 et 6 pour une comparaison à pH 3). La seconde vague B correspond, d'après son potentiel de réduction, à la réduction de la fonction *N*-oxyde. Pour les formylpyridine-2 et -4 *N*-oxydes, cependant, la hauteur anormalement grande de la vague en milieu très acide montre qu'il ne peut s'agir de la réduction simple de la fonction carbonyle qui présente normalement une vague à 2*F* seulement. Cette anomalie nous a incités à examiner en premier lieu de façon approfondie le mécanisme de la réduction. La différence de comportement entre le dérivé 3 d'une part et les dérivés 2 et 4, d'autre part, conduit d'ailleurs à envisager deux mécanismes différents. Nous exposerons ensuite les résultats concernant les phénomènes d'hydratation.

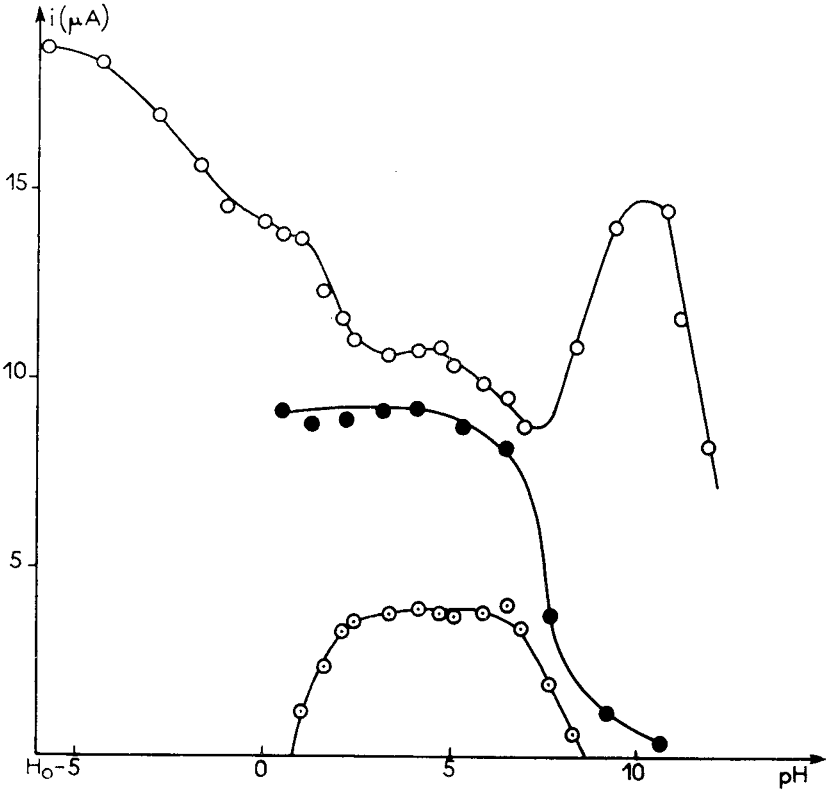
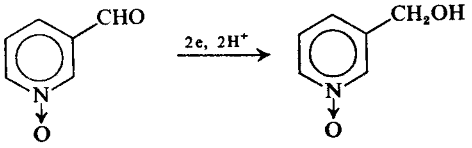


FIG. 2.—Variation du courant limite en fonction du pH.
Formyl-4 pyridine *N*-oxyde: ○, vague A, ou somme des vagues A_1' et A_2', ou A_1 et A_2; ⊙, vague B.
Hydroxyméthyl-4 pyridine *N*-oxyde: ●.

MECANISME DE REDUCTION

Formylpyridine-3 N-*oxyde*

Vague A. Cette vague correspond à la réduction normale de la fonction carbonyle, en hydroxyméthyl-3 pyridine *N*-oxyde, suivant le schéme global:



(I)

En milieu acide, la réaction électrochimique peut d'ailleurs être précédée de façon normale d'une préprotonisation de la fonction aldéhyde et de la fonction *N*-oxyde.

Ce mécanisme a été vérifié par électrolyse à potentiel contrôlé: (*a*) une coulométrie (pH 5,1) montre que la réduction fait bien intervenir 2*F* (tableau I); (*b*) après électrolyse totale de la solution, on enregistre le spectre U.V. de la solution à diverses valeurs du pH; ce spectre est identique à celui de l'hydroxyméthyl-3 pyridine *N*-oxyde, et les valeurs du p*K* déterminées à partir des spectres sont identiques (tableau II).

Vague B. Cette vague, due à la réduction de la fonction *N*-oxyde protonisée,[1] se compose en réalité de deux vagues confondues: (*a*) la première correspond à la

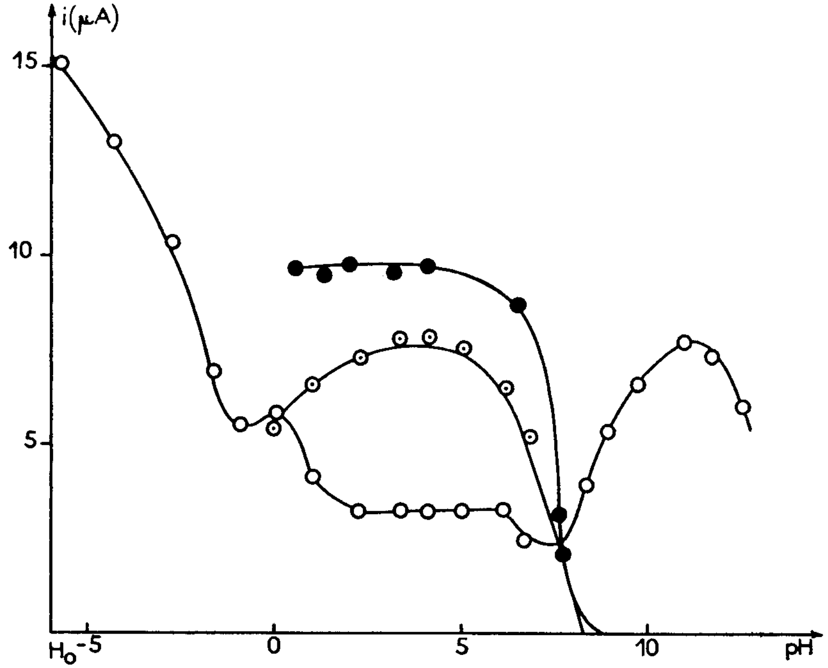


FIG. 3.—Variation du courant limite en fonction du pH.
Formyl-2 pyridine *N*-oxyde: ○, vague A, ou somme des vagues A_1 et A_2; ⊙, vague B.
Hydroxyméthyl-2 pyridine *N*-oxyde: ●.

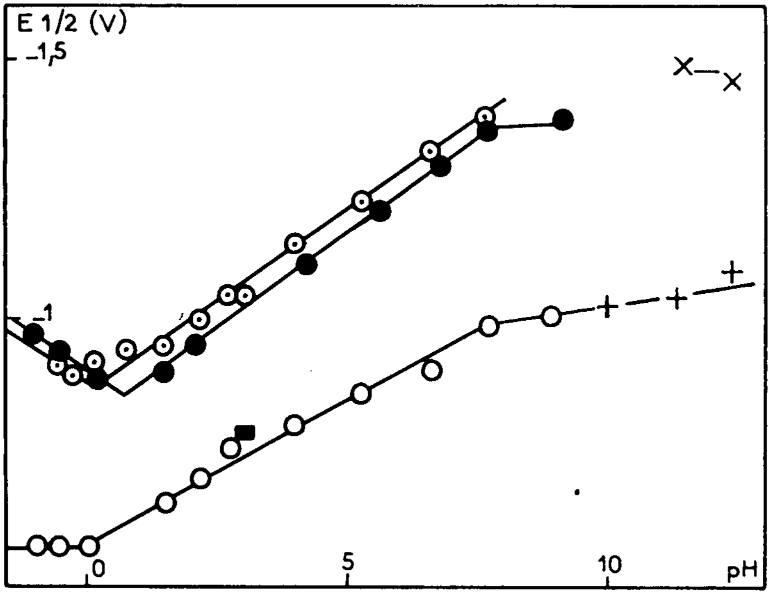


FIG. 4.—Variation de $E_{1/2}$ en fonction du pH.
Formyl-3 pyridine *N*-oxyde: ○, vague A; +, vague A_1; ×, vague A_2; ⊙, vague B.
Hydroxyméthyl-3 pyridine *N*-oxyde: ●.
Formyl-3 pyridine: ■.

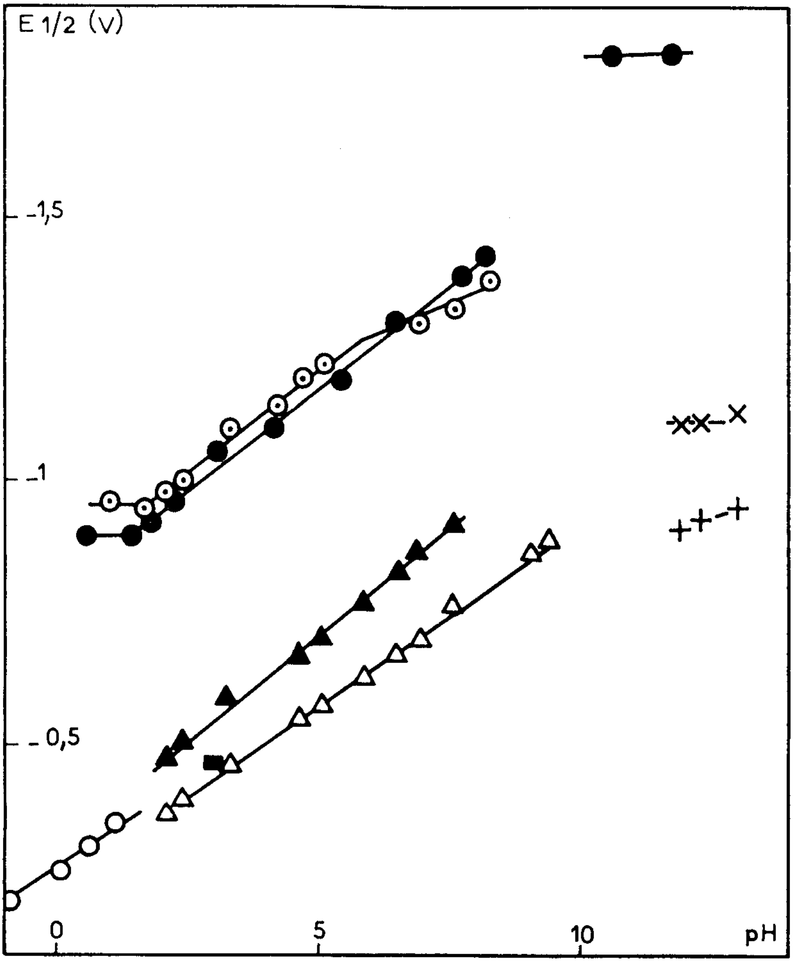
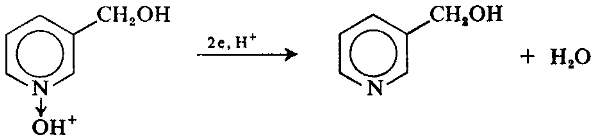
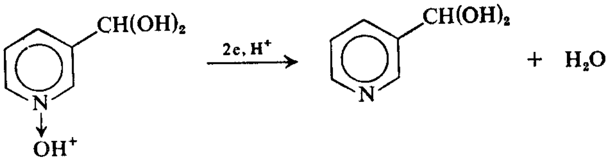


FIG. 5.—Variation de $E_{1/2}$ en fonction du pH.
Formyl-4 pyridine *N*-oxyde: ○, vague A; △, vague A_1'; ▲, vague A_2'; +, vague A_1; ×, vague A_2; ⊙, vague B.
Hydroxyméthyl-4 pyridine *N*-oxyde: ●.
Formyl-4 pyridine: ■.

réduction de la fonction *N*-oxyde de l'alcool obtenu au premier stade de la réduction (schéma II) et conduit à l'hydroxyméthyl-3 pyridine; (*b*) la seconde correspond à la réduction de la fonction *N*-oxyde de l'hydrate d'aldéhyde, suivant le schéma III:



(II)



(III)

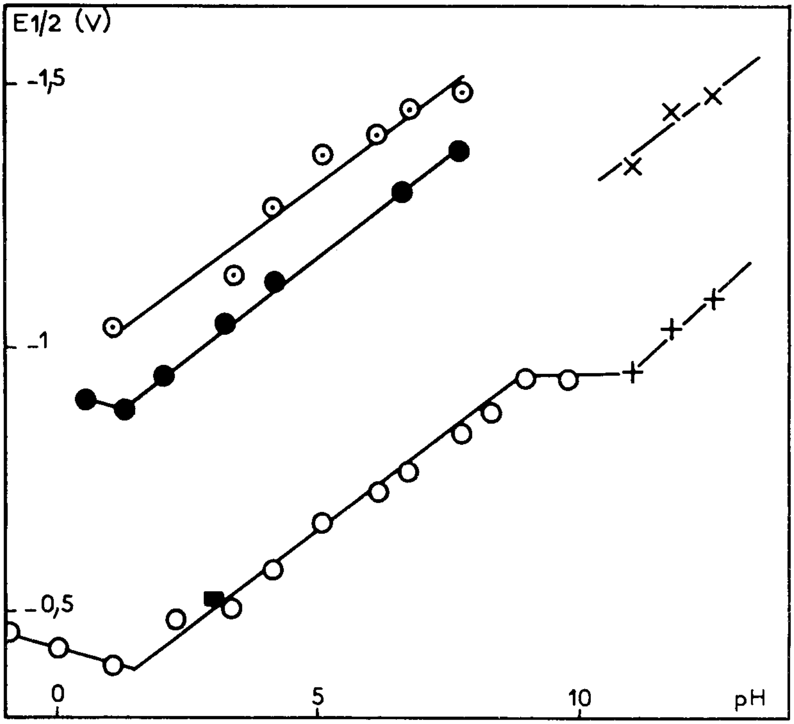


FIG. 6.—Variation de $E_{1/2}$ en fonction du pH.
Formyl-2 pyridine *N*-oxyde: ○, vague A; +, vague A_1; ×, vague A_2; ⊙, vague B.
Hydroxyméthyl-2 pyridine *N*-oxyde: ●.
Formyl-2 pyridine: ■.

TABLEAU I.—COULOMÉTRIES

Composé	Vague	Potentiel, *V*	pH	*F* trouvé	*F* théorique
Formylpyridine-3 *N*-oxyde	A	−1,00	5,1	2,07	2
	B	−1,45	5,1	4,3	4
Formylpyridine-4 *N*-oxyde	A	−0,85	4,05	3,89	4
	A_2	−1,40	11,9	1,76	
	A_1	−1,05	11,9	1,08	

TABLEAU II.—PRÉPARATIONS À POTENTIEL CONTRÔLÉ

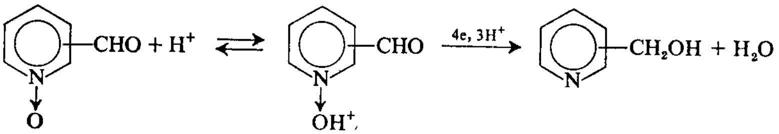
Composé	Vague	Potentiel, *V*	pH	pK_a	pK_a du composé posé de référence	Composé de référence	Comparaison du spectre avec celui du composé de référence
Formylpyridine-3 *N*-oxyde	A	−1,05	5,1	0,65	0,60	hydroxyméthyl-3 pyridine *N*-oxyde	spectres U.V. identiques
	B	−1,45	5,1	5,0	4,9	hydroxyméthyl-3 pyridine	spectres U.V. identiques
Formylpyridine-4 *N*-oxyde	A	−0,60	1,0			chlorhydrate d'hydroxyméthyl-4 pyridine	spectres I.R. identiques
	A_2	−1,40	11,9	0,6			

L'effet électronique des groupements CH_2OH et $CH(OH)_2$ est faible; ceci explique que les deux vagues soient confondues, bien que la loi de Hammett appliquée aux potentiels de demi-vague des pyridine *N*-oxydes substitués conduise à une valeur de ρ assez élevée ($\rho \simeq 0,5$ V).[2]

Formylpyridine-2 *et* -4 N-*oxydes*

Vague A, milieu acide (pH < 6 *environ*). Pour interpréter la hauteur anormale de la première vague en milieu acide, la seule hypothèse vraisemblable était celle d'une réduction simultanée des fonctions carbonyle et *N*-oxyde, bien qu'habituellement les potentiels de réduction de la fonction *N*-oxyde se situent à des valeurs beaucoup plus négatives.[1,2]

En milieu acide, la réduction conduit à l'hydroxyméthylpyridine, suivant le schéma global:



(IV)

Ce mécanisme a été confirmé par électrolyse à potentiel contrôlé et par coulométrie. Une coulométrie effectuée à pH 4,05 sur la première vague A de réduction du formylpyridine-4 *N*-oxyde montre que la réduction consomme 4*F* (tableau I). Après une électrolyse en milieu chlorhydrique sur la vague A, on peut isoler un chlorhydrate dont le spectre I.R. a été comparé à celui du chlorhydrate de l'hydroxyméthyl-4 pyridine. Les spectres sont identiques (tableau II). Lors de ces électrolyses, la deuxième vague B disparaît simultanément à la première. Comme nous le verrons plus loin, la deuxième vague est due à la réduction de la fonction *N*-oxyde de l'hydrate. Au fur et à mesure de la réduction sur la première vague, l'hydrate se transforme en aldéhyde libre qui subit la réduction totale des deux fonctions, ce qui explique la disparition de la seconde vague.

Vague A, milieu basique (pH > 9 *environ*). L'interprétation des polarogrammes en milieu alcalin est rendue délicate par la coexistence de divers phénomènes: la recombinaison donnant naissance à la surface de l'électrode à la forme protonisée du *N*-oxyde[1] n'a plus lieu. Dans cette région cesse sans doute aussi le phénomène de protonisation de la fonction carbonyle. Enfin, les phénomènes d'hydratation perturbent le courant. Il semble cependant, d'après les résultats de l'électrolyse à potentiel contrôlé, que la réduction de la fonction *N*-oxyde n'aurait plus lieu simultanément à celle de la fonction carbonyle. En milieu basique, la vague A est scindée en deux vagues A_1 et A_2 d'égale hauteur. Une coulométrie, effectuée sur la vague A_1 à pH 12, montre que la réduction consomme 1*F* (tableau I). Au cours de l'électrolyse, la vague A_2 diminue simultanément à la vague A_1. La solution obtenue après électrolyse complète a été polarographiée à différents pH; on obtient une vague dont le potentiel et les caractéristiques correspondent à la réduction d'une fonction *N*-oxyde.

Une coulométrie effectuée sur le plateau de la vague A_2 montre que la réduction consomme 2*F* (tableau I). La solution obtenue après électrolyse complète a été étudiée par spectroscopie U.V. La valeur du p*K* du produit d'électrolyse, déterminée à partir des spectres, est égale à 0,6 (tableau II). Une étude polarographique de la même solution fait apparaître entre pH 0,5 et 10 une vague dont les $E_{\frac{1}{2}}$ se situent dans le domaine de réduction de la fonction *N*-oxyde.

Il n'a pas été possible d'identifier le produit obtenu par réduction sous potentiel contrôlé, en raison des faibles quantités mises en jeu. Il semble cependant, d'après les résultats précédents, que la fonction *N*-oxyde ne soit pas réduite sur la vague A en milieu alcalin. Les vagues A_1 et A_2 correspondent donc sans doute respectivement à la réduction du carbonyle en pinacol et en alcool.

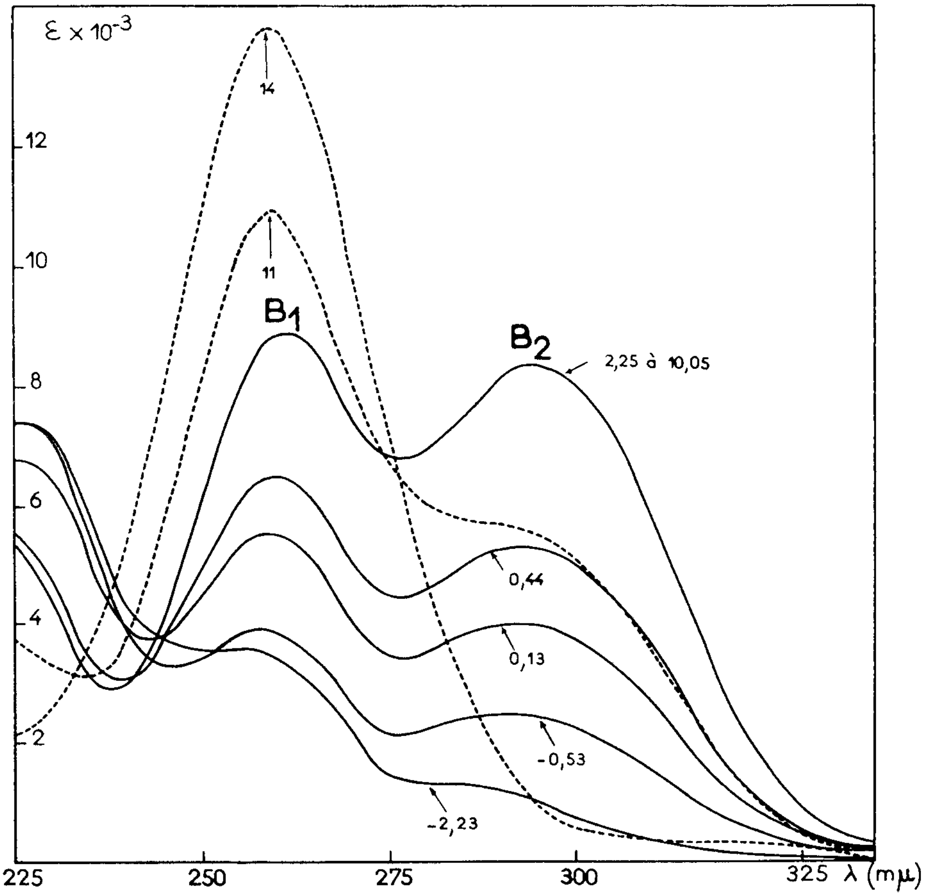
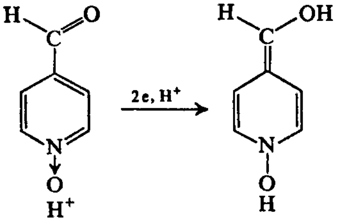


FIG. 7.—Spectre U.V. du formyl-4 pyridine *N*-oxyde.
Sur cette figure et sur les deux suivantes, les valeurs du pH ou de la fonction d'acidité de Hammett H_0 sont indiquées sur les courbes.

Nous avons d'ailleurs pu mettre en évidence de façon beaucoup plus nette un changement du mécanisme de réduction dans le cas des oximes correspondantes:[4] en milieu acide, il y a réduction simultanée des fonctions oxime et *N*-oxydes alors qu'en milieu alcalin, seule se réduit la fonction oxime. Une étude des acétylpyridine *N*-oxydes[5] devrait d'ailleurs permettre également de préciser le mécanisme de réduction.

Interprétation du mécanisme de réduction en milieu acide. On peut remarquer que la réduction simultanée de la fonction *N*-oxyde et de la fonction aldéhyde n'a lieu que pour les dérivés 2 et 4, et ne concernent que la forme protonisée du *N*-oxyde: le formyl-3 pyridine *N*-oxyde se réduit normalement ainsi que la forme non protonisée des formyl-2 et 4 pyridines.

Compte tenu de ces données, on peut penser que la réduction (schéma IV) ferait intervenir intermédiairement une forme quinoïde, qui n'est possible que dans le cas où le carbonyle est en position 2 ou 4. On aurait par exemple:



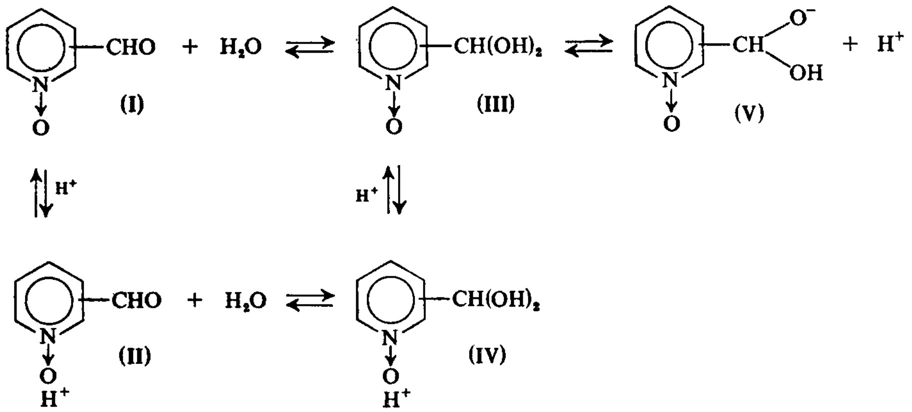
Cette forme quinoïde ne peut exister dans le cas où le carbonyle se trouve en position 3, et ne se formerait plus lorsque la fonction *N*-oxyde n'est pas protonisée.

La scission de la vague A du formylpyridine-4 *N*-oxyde en deux vagues A_1' et A_2' est en bon accord avec une hypothèse de ce type. On ne peut envisager en effet une réduction successive des deux fonctions suivant les vagues A_1' et A_2': (*a*) si A_1' correspondait à la réduction de la fonction *N*-oxyde, la vague A_2' serait la vague de réduction de la formylpyridine correspondante; or le potentiel de A_2' est plus négatif que celui de la formylpyridine; (*b*) si A_1' correspondait à la réduction de la fonction aldéhyde, la vague A_2' serait la vague de réduction de la fonction *N*-oxyde du pyridine méthanol *N*-oxyde, et devrait se trouver à des potentiels beaucoup plus négatifs. Il faut donc faire appel à un mécanisme de réduction global pour interpréter la réduction.

Vague B. La vague B correspond à la réduction de la fonction *N*-oxyde de *l'hydrate d'aldéhyde* suivant le schéma III. La réduction du *N*-oxyde de l'alcool, qui venait se superposer à celle de l'hydrate dans le cas du formylpyridine-3 *N*-oxyde, n'a pas lieu ici: comme nous venons de le voir, la réduction sur la première vague conduit en effet directement à l'hydroxyméthylpyridine correspondante. La hauteur anormalement faible de la vague, liée au phénomène d'hydratation sera interprétée plus loin.

PHENOMENE D'HYDRATATION

Comme dans le cas des formylpyridines,[3] cinq formes peuvent exister en solution et donner lieu aux équilibres:



Avant d'examiner l'influence de l'hydratation sur les polarogrammes, nous exposerons les résultats de l'étude par spectroscopie U.V.

Etude spectroscopique

De façon générale, le spectre U.V. des pyridines *N*-oxydes est très semblable à celui des bases pyridiniques correspondantes.[6] Le comportement des formylpyridines *N*-oxydes est conforme à cette règle: on observe, comme dans le cas des formylpyridines,[3] trois bandes d'absorption principales, la bande K, la bande B d'absorption benzénoïde et la bande R du carbonyle. Nous n'étudierons que les bandes B et R.

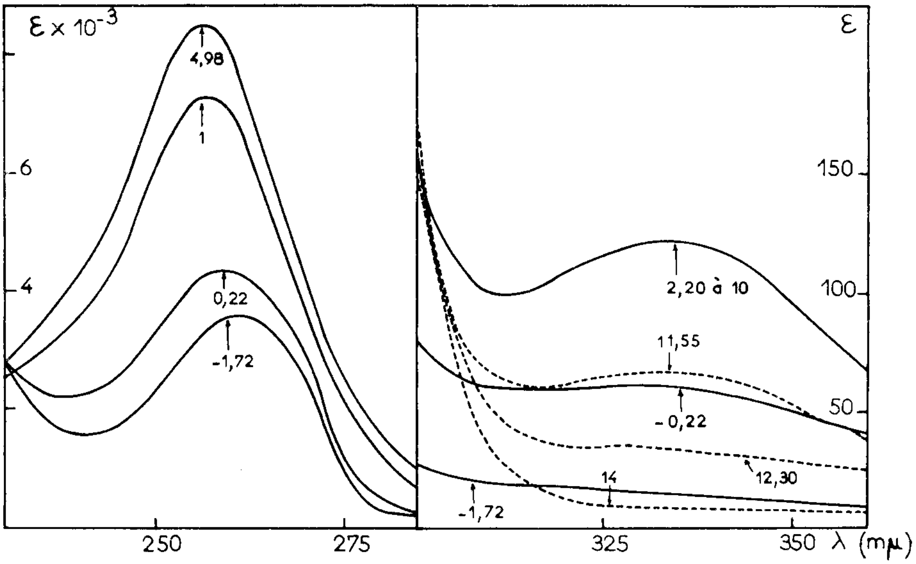


FIG. 8.—Spectre U.V. du formyl-2 pyridine *N*-oxyde.
à gauche: bande B; à droite: bande R.

Bande B. Pour les formylpyridines-2 et -3 *N*-oxydes, comme pour les formylpyridines correspondantes, la bande B de l'hydrate et celle de l'aldéhyde libre sont très voisines et ne peuvent être distinguées (Fig. 8 et 9). Pour le formylpyridine-4 *N*-oxyde, au contraire, la bande B se dédouble, comme pour la formylpyridine-4,[3] en deux bandes B_1 et B_2 (Fig. 7): la bande B_1 est la bande benzenoïde de la forme hydratée (formes **III** et **IV**) et se trouve à des longueurs d'onde voisines de celle du pyridine *N*-oxyde, et la bande B_2 celle de la forme carbonyle libre (formes **I** et **II**). Le déplacement bathochrome considérable de la bande B_2 par rapport à celle du pyridine *N*-oxyde est dû à la présence du groupe CHO et est du même ordre de grandeur que dans le cas de la formyl-4 pyridine.[3] Cette séparation en deux bandes permet ici encore d'estimer le taux d'hydratation aux différents pH (Fig. 10): en milieu neutre, l'intensité des deux bandes est à peu près égale et le taux d'hydratation est donc d'environ 50%.

En milieu acide la bande B de tous les composés évolue par suite de la protonisation de la fonction *N*-oxyde et il est possible de déterminer le pK_A (pK apparent, cf. réf. 3) correspondant (tableau III).

En milieu alcalin, on observe également une évolution, due à l'ionisation de

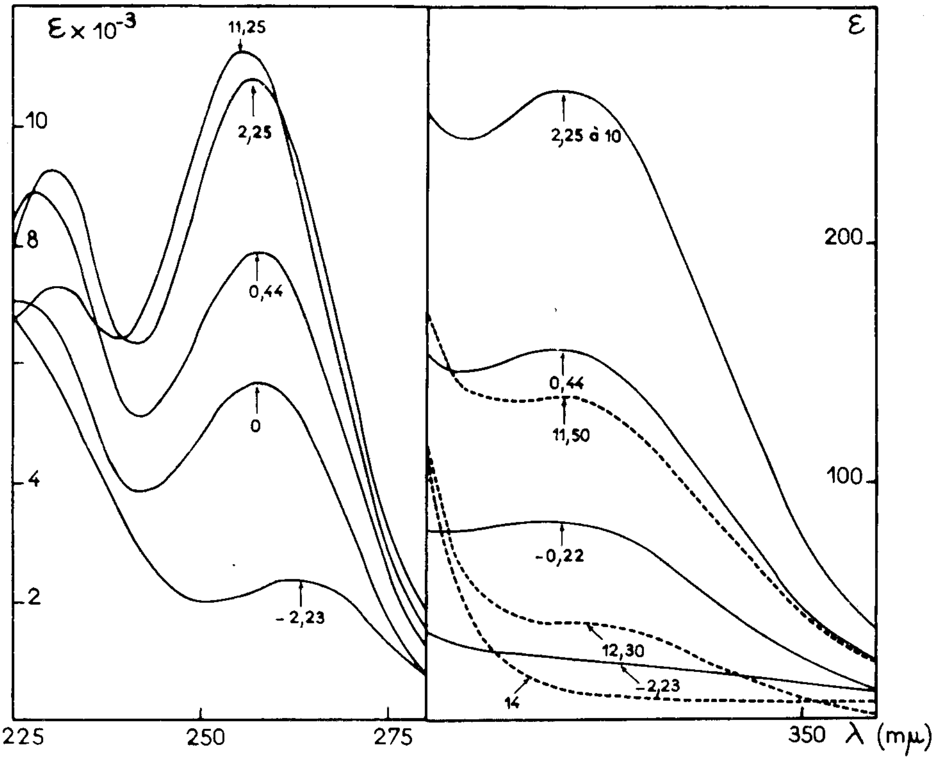


FIG. 9.—Spectre U.V. du formyl-3 pyridine *N*-oxyde.
à gauche: bande B; à droite: bande R.

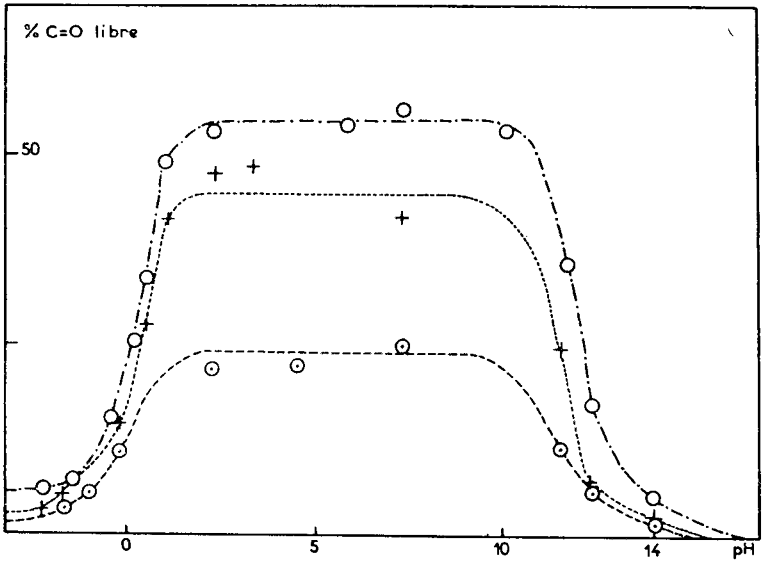


FIG. 10.—Graphique donnant le taux approximatif de carbonyle libre en fonction du pH.
⊙: formyl-2 pyridine *N*-oxyde; +: formyl-3 pyridine *N*-oxyde;
○: formyl-4 pyridine *N*-oxyde.

l'hydrate d'aldéhyde (équilibre entre les formes III et V). Cette évolution permet ici encore de déterminer une valeur de pK. Ce pK est encore un pK apparent, qui ne correspond pas au pK de l'équilibre précédent, et que nous avons désigné par pK'_A (tableau III).

En milieu alcalin, seules existent les formes I, III et V. Si on désigne par K_a la constante de l'équilibre d'ionisation.

$$K_a = \frac{[V][H^+]}{[III]}$$

et par K_1 la constante de l'équilibre d' hydratation

$$K_1 = \frac{[I]}{[III]}$$

on peut calculer facilement la relation:

$$K_A' = \frac{K_a}{1 + K_1}$$

Les valeurs de K_A' sont assez voisines de celles obtenues pour les formylpyridines.[7,8] Une étude en fonction du temps nous a permis de constater que les formylpyridines *N*-oxydes sont stables en milieu alcalin: le spectre ne subit aucune évolution en l'intervalle d'une heure.

Bande R. La bande R d'absorption du carbonyle n'apparaît distinctement que dans le cas des formylpyridines-2 et -3 *N*-oxydes (Fig. 8 et 9). Pour le dérivé 4 elle est masquée par la bande B beaucoup plus intense. La bande R permet de suivre directement l'hydratation en fonction du pH. Comme on peut le constater, l'hydratation est plus forte pour le dérivé 2 que pour le dérivé 3. On pourra ici encore, en tenant compte des résultats de l'étude polarographique, tracer les courbes donnant approximativement le taux d'hydratation (Fig. 10).

Dans le tableau III figurent les valeurs des différents pK, déterminés à partir des spectres.

TABLEAU III.—pK DES FORMYLPYRIDINES *N*-OXYDES.

Position du CHO	pK_A	pK_A'
2	0,25	11,40
3	0,22	11,70
4	0,30	12,15

Etude polarographique

Les résultats de l'étude spectrophotométrique ont montré: (*a*) que les pK_A des formylpyridines *N*-oxydes sont de l'ordre de 0,3; (*b*) que l'hydratation, moyenne en milieu neutre, devient très forte en milieu acide, et pratiquement totale en milieu alcalin, par suite du déplacement de l'équilibre d'ionisation de l'hydrate d'aldéhyde: en milieu alcalin, tout l'aldéhyde se trouve sous forme V.

Compte tenu de ces résultats et du mécanisme de la réduction, il est possible d'interpréter les variations du courant limite en fonction du pH (Fig. 1, 2 et 3).

Milieu acide (pH < 5 environ), *vague A*. La zone d'équilibre acidobasique (pour sa définition, voir réf. 3) dans laquelle le courant devrait décroître par suite de l'hydratation de plus en plus intense liée à la protonisation de la fonction *N*-oxyde, est déplacée vers les pH acides ($pK_A \sim 0$) par rapport à la série pyridinique. Cette zone tombe alors au début de la zone de catalyse acide,[3] où le courant croît par suite d'une accélération de la vitesse de déshydratation (courant cinétique). La variation du courant peut s'interpréter de la façon suivante: la catalyse acide provoque une augmentation du courant dès pH 2; vers pH 0 on atteint la zone d'équilibre acidobasique, dans laquelle il y a une augmentation du taux d'hydratation. Il en résulte pour le courant total une légère diminution (formylpyridines-2 et -3 *N*-oxydes) ou un palier (formylpyridine-4 *N*-oxyde) (Fig. 1, 2 et 3).

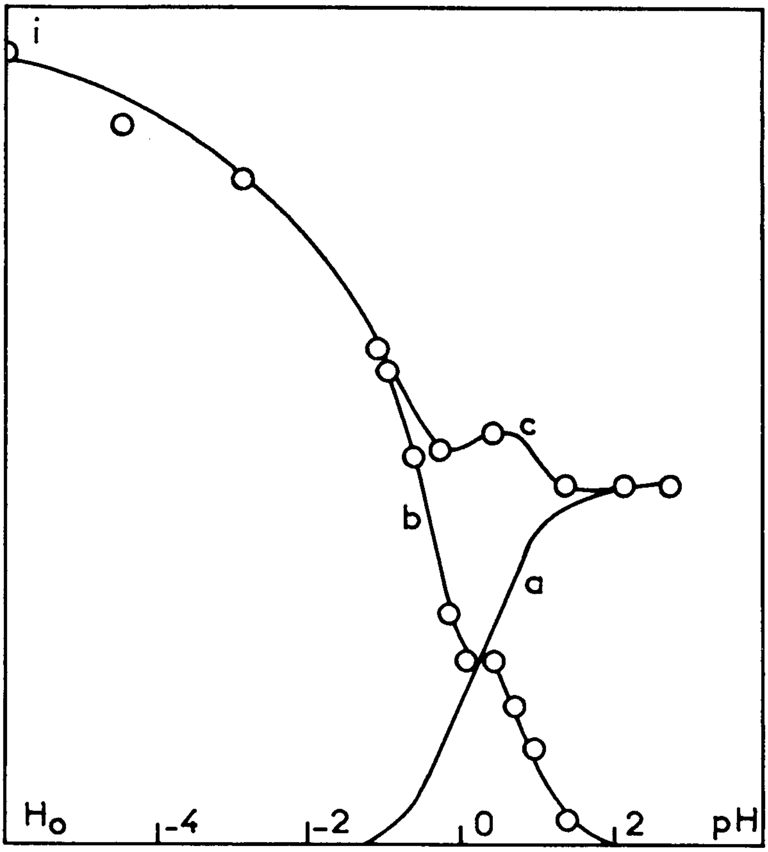


Fig. 11.—Variation schématique du courant limite en milieu acide (cas du formyl-3 pyridine *N*-oxyde).
c: courbe expérimentale; *a*: courbe théorique calculée à l'aide de l'équation (19) de la référence 3, en supposant $i_m = 0$; *b*: courbe obtenue par différence entre *c* et *a*.

La variation schématique des diverses composantes du courant est indiquée sur la figure 11. La courbe d'équilibre acidobasique (courbe *a*) a été calculée au moyen de l'équation (19) de la référence 3, en supposant $i_m = 0$. On remarquera que la variation du courant cinétique (courbe *b*) est analogue à celle observée dans le cas des formylpyridines, mais que la courbe semble constituée de deux parties. Ceci peut sans doute s'expliquer par le fait qu'au début de la courbe (pH 2 à 0) la catalyse porte sur la réaction de déshydratation de la molécule d'hydrate neutre (forme III), alors qu'en milieu plus acide ($H_0 < 0$), la catalyse porte sur la réaction de déshydratation de la molécule d'hydrate protonisée (forme IV). Dans le cas des formylpyridines, il s'agissait toujours d'une molécule chargée positivement.[3]

Milieu acide, vague B. Comme nous l'avons établi plus haut, cette vague est due à la réduction de la fonction *N*-oxyde. Dans le cas du *formylpyridine*-3 *N-oxyde*, la vague B est composée des vagues de réduction de la fonction *N*-oxyde de l'hydrate et de l'alcool apparu au cours de la réduction sur la vague A. Sa hauteur devrait donc rester constante à tous les pH, puisque la concentration totale de ces deux formes aux abords de l'électrode est toujours égale à la concentration analytique. Comme le montre la figure 1, on observe cependant vers pH 1 un minimum sur la courbe $i = f(\text{pH})$. Ce phénomène peut s'interpréter de la façon suivante: les vagues relatives à l'hydrate et à l'alcool ne seraient confondues que pour pH 1. En dessous de pH 1, la vague relative à l'hydrate ne serait plus observable, à cause de la proximité de la décharge des ions hydrogènes; seule subsisterait alors la vague relative à l'alcool. Cette vague augmenterait ensuite normalement pour $H_0 < 0$, parallèlement à la première vague A, puisque la quantité d'alcool qui se forme à la surface de l'électrode est de plus en plus grande.

Pour les formylpyridines-2 et -4 *N*-oxydes, nous avons montré plus haut que la deuxième vague B est due uniquement à la réduction de la fonction *N*-oxyde de l'hydrate. La vague est donc d'autant plus haute que l'hydratation est plus forte. Cette interprétation est confirmée par l'examen des graphiques $i = f(\text{pH})$ (Fig. 2 et 3) et en particulier par le fait que la vague est beaucoup plus haute pour le formylpyridine-2 *N*-oxyde que pour le formylpyridine-4 *N*-oxyde qui est moins hydraté.

La diminution de la vague B en milieu acide est liée à la diminution de la quantité d'hydrate à la surface de l'électrode, puisque dans cette zone le courant catalytique correspond à une augmentation du nombre de molécules réduites directement en hydroxyméthylpyridine, donc à une diminution des molécules de forme hydratée. En dessous de pH 0 environ, la vague n'est plus discernable à cause du courant de décharge des ions hydrogènes.

Milieu neutre et alcalin (pH > 5 environ), *vague A.* Dans le cas du *formylpyridine*-3 *N-oxyde*, le courant augmente dès pH 7, par suite d'une catalyse basique de déshydratation.[3] Vers pH 11, la vague décroît à nouveau; cette décroissance est attribuable à la dissociation de l'hydrate d'aldéhyde, qui provoque un déplacement de l'équilibre en faveur de la forme hydratée.

Pour les formylpyridines-2 et -4 *N*-oxydes, on observe encore vers pH 8 l'augmentation du courant due à la catalyse basique, suivie d'une diminution rapide à partir de pH 11. Cependant, entre pH 5 et 8 environ, la hauteur de la vague A diminue parallèlement à celle de la fonction *N*-oxyde. Cette diminution est sans doute liée au changement de mécanisme de la réduction qui a tendance à consommer $2F$ au lieu de $4F$ lorsque le pH augmente.

Milieu neutre et alcalin, vague B. La vague B, qui représente la réduction du groupe *N*-oxyde protonisé, disparaît dans tous les cas vers pH 10, conformément au mécanisme général de réduction des *N*-oxydes.[1] La vague de réduction du *N*-oxyde non protonisé n'apparaît que dans le cas du dérivé 4 (Fig. 5).

PARTIE EXPERIMENTALE

Polarographie

Les polarogrammes ont été enregistrés sur un polarographe Radiometer PO 4. Le capillaire présentait les caractéristiques suivantes: $m = 2{,}54$ mg/sec; $t = 3{,}5$ sec en circuit ouvert. Les mesures ont été effectuées en milieu aqueux (tampons Britton-Robinson; NaOH; $HClO_4$). La concentration analytique en dépolarisant était de 10^{-3} *M*.

Pour des solutions très acides $H_0 < 0$, la diminution de la hauteur de la vague due à l'augmentation de la viscosité a été corrigée en tenant compte des valeurs de la viscosité des mélanges $HClO_4$–H_2O indiqués dans la littérature.[9]

Potentiel contrôlé

Les électrolyses ont été effectuées sur nappe de mercure, le potentiel étant maintenu constant au moyen de potentiostats Tacussel ASA 4/60 ou ASA 100. Pour la coulométrie, la concentration en substance était de $2.10^{-3}M$. Lors des réductions préparatives, la concentration était de 10^{-2} *M*. Les mesures coulométriques ont été effectuées soit par intégration graphique des courbes $I = f(t)$, soit au moyen d'un intégrateur Tacussel IG 3.

Spectrophotométrie

Pour les spectres U.V. on a utilisé un spectrophotomètre Beckmann DK 2. Les solutions étaient tamponnées au moyen des mêmes tampons qu'en polarographie. Les spectres I.R. ont été tracés au moyen d'un appareil Beckmann I.R. 8.

Synthèse des produits étudiés

Les formylpyridines *N*-oxydes ont été préparés d'aprés les données de la littérature,[10] par oxydation des alcools correspondants.

Summary—The 2- and 4-formylpyridine *N*-oxides show, in acid medium, an abnormal reduction mechanism. The first wave, with a potential which lies in the neighbourhood of the usual value for the aldehyde group, is due to the simultaneous reduction of the *N*-oxide group and the carbonyl group. The second wave is due to the reduction of the *N*-oxide group in the presence of a hydrated aldehyde group. 3-Formylpyridine *N*-oxide is reduced normally at all pH values, with the reduction of the carbonyl group preceding that of the *N*-oxide group. The reduction mechanisms have been verified by controlled potential electrolysis. The hydration of the carbonyl group has been studied by polarographic and spectrophotometric methods.

Zusammenfassung—Die *N*-Oxide von 2- und 4-Formylpyridin zeigen in saurem Medium einen anormalen Reduktionsmechanismus. Die erste Stufe mit einem Potential in der Nähe des üblichen Wertes für die Aldehydgruppe rührt von der gleichzeitigen Reduktion der *N*-Oxidgruppe und der Carbonylgruppe. Die zweite Stufe kommt von der Reduktion der *N*-Oxidgruppe in Gegenwart einer hydratisierten Aldehydgruppe. 3-Formylpyridin-*N*-oxid wird bei allen pH-Werten normal reduziert, wobei die Reduktion der Carbonylgruppe der der *N*-Oxidgruppe vorangeht. Die Reduktionsmechanismen wurden durch Elektrolyse bei kontrolliertem Potential verifiziert. Die Hydratation der Carbonylgruppe wurde polarographisch und spektrophotometrisch untersucht.

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A CHEMICAL CONCENTRATION X-RAY DETERMINATION OF SELENIUM IN COPPER-, NICKEL- AND IRON-BASE ALLOYS*

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Summary—A method is described for the determination of selenium in various metals and alloys at concentrations of 3–100 ppm. A chemical separation is made by filtration after reduction of the selenious acid to elemental selenium with hydroxylamine hydrochloride. The pure selenium product is readily analysed by X-ray fluorescence; the method is free from errors due to matrix effects. The relative standard deviation is 6% for a copper–nickel alloy at the 60 ppm level.

SELENIUM is commonly present in trace amounts in metals and alloys, sometimes occurring as a residual impurity. In some instances small quantities of selenium are added in order to impart beneficial physical and mechanical properties. The analysis for small amounts of selenium frequently involves chemical separation of it from the matrix by reduction to its elemental form, and filtration.[1] The final determination is then made by titration with thiosulphate. Selenium is also determined by spectrophotometric methods in which its *o*-phenylenediamine or 3,3′-diaminobenzidine complex is extracted into an organic solvent such as toluene.[2,3] X-Ray spectroscopy is sometimes used for the direct determination of selenium but it is not sensitive to concentrations below about 0·02%.[4] A rapid chemical procedure for the concentration of selenium would make the X-ray method useful for analysis of materials which contain less than 100 ppm of selenium, and ideally should be applicable to dissimilar matrices. One limitation to the X-ray method is that the intensity of the characteristic secondary radiation is not in simple proportion to the quantity of element. This lack of proportionality results from absorption and enhancement, and may be eliminated by first separating the element and placing it in a very thin layer beneath the X-ray beam.[5] It is our aim to apply an X-ray fluorescence method to the determination of selenium, after it has been reduced to the element and separated from its matrix.

EXPERIMENTAL

Reagents

Standard selenium solutions. Dissolve 0·5000 g of 99·99% pure selenium in 10 ml of concentrated nitric acid and dilute to 1 litre with water. Prepare a selenium solution containing 10 μg/ml by diluting 10 ml of this stock solution to 500 ml with water.

Other reagents should be analytical grade.

Apparatus

Microfiltration apparatus. A Millipore (Bedford, Mass.) filtration assembly No. XX100 2500, containing a suction flask, micro funnel, sintered glass disc and clamps. Micropore filters (GS WPO

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2500) of 0·22 μ pore-size and 25 mm diameter. Glass fibre filters (No. 934AH, Reeve Angel, Clifton, N.J.).

X-Ray spectrograph. An XRD-6 General Electric X-ray spectrograph was used with an EA-75 platinum target tube, lithium fluoride crystal, and 0·25 × 100 mm collimator. The tube was operated at a power of 50 mA and 50 kV. A combination scintillation (SPG-4) and flow (SPG-7) counter was used with a mixture of argon and methane (P-10 gas). The sample drawer mask and mounts for the sample filters were made of 3-mm thick phenol fabric.

Procedure

Dissolution. Transfer an accurately weighed representative sample to a 150-ml beaker and treat it with 5 ml of perchloric acid and 25 ml of nitric acid. (This acid mixture is designed for sample weights of 1 g or less.) Cover the beaker with a watch-glass and digest on a hot-plate at moderate heat until the reaction is complete. Continue heating until the nitric acid has been removed by volatilization. Cool to room temperature, then add 75 ml of 6*M* hydrochloric acid. (Digest at a moderate heat to dissolve the salts.) Filter the solution through a glass fibre filter attached to the microfiltration apparatus. Wash the filter and residue thoroughly with 6*M* hydrochloric acid.

Reduction and separation. Return the prefiltered solution to the 150-ml beaker, add 4 g of hydroxylamine hydrochloride, and cover with a watch-glass. Boil for 2–5 min. Cool to room temperature and filter off on a 0·22-μ micropore filter. Wash the filter and selenium with water. Air-dry the filter for about 1 hr and then mount it on a phenol fabric disc with double-backed adhesive.

X-Ray analysis. Position the mounted samples in the sample drawer of the spectrograph and measure the K_α radiation for 10 sec at $2\theta = 31{\cdot}89°$. Obtain a background correction by making similar measurements on a blank filter disc. Calculate the concentration of selenium by using a factor obtained by analysing a series of standards containing 5–100 μg of selenium.

DISCUSSION

The acid dissolution of a metal or alloy to be analysed for selenium serves the dual purpose of decomposing the metal selenide and converting the selenium into selenious acid, a form in which it is readily reduced to the elemental form. A potential source of error in the dissolution may be loss of selenium as the volatile $SeO_2{\cdot}2HCl$ or as Se_2Cl_2. It is also possible to volatilize selenium as hydrogen selenide if a non-oxidizing acid is used alone for dissolution. The samples analysed were dissolved in a 1:5 mixture of perchloric and nitric acids. After dissolution was complete the solutions were fumed with perchloric acid to remove nitric acid. To verify that little or no selenium was lost in this heating, 500 μg of selenium were heated with perchloric acid for 3 and 5 min periods. Only 1·2% was lost by volatilization when heated for 5 min at 185–200°. This was in agreement with the work of Bock and Jacob.[6]

After removal of nitric acid the solution was diluted and filtered to remove those elements which are hydrolysed in strongly acid solutions, *e.g.*, niobium, silicon, tantalum and tungsten, and will interfere in the X-ray measurement by causing absorption or enhancement of the selenium radiation. Noble metals would also be a source of error as they would be reduced by hydroxylamine along with selenium. One possible answer would be to use ascorbic acid[7] which will precipitate selenium but not the noble metals.

Selenium and tellurium often occur together, but only selenium is reduced by sodium sulphide, hydroxylamine hydrochloride, hydrazine and ascorbic acid. Hydroxylamine hydrochloride was used in this work because it completely and rapidly precipitates selenium in a pure form from strongly acid solution. The optimum conditions were found as shown in Table I. Complete precipitation of 100 μg of selenium was obtained when 4 g of hydroxylamine hydrochloride were heated for 2–5 min with 100 ml of a solution which was 2–8*M* in hydrochloric acid.

TABLE I.—EVALUATION OF CONDITIONS FOR COMPLETE PRECIPITATION OF SELENIUM WITH HYDROXYLAMINE HYDROCHLORIDE

$NH_2OH \cdot HCl$, *g*	[HCl], *M*	Boiling time, *min*	Se, *μg* Added	Se, *μg* Found
2	6	15	100	96
4	6	15	100	100
2	6	15	1000	795
4	6	15	1000	925
8	6	15	1000	1000
4	6	0	100	31
4	6	1	1000	1004
4	6	2	1000	979
4	6	20	100	100
4	0·1	15	100	75
4	0·5	15	100	94
4	2	15	100	102
4	4	15	100	100
4	6	15	100	102
4	8	15	100	101
4	11	15	100	19

The reduced selenium was filtered as previously described for tellurium.[8] Freshly reduced elemental selenium is red, finely divided, amorphous, and sometimes colloidal, so filters of various porosity were tried, to determine their retention. It was shown that 2–3 μg of a 20-μg sample will pass through an 8-μ pore filter but all of the selenium is retained on a 0·22-μ pore filter. Newberry and Christian[7] used a filter with a 0·8-μ pore size and found quantitative retention of as little as 1 μg of selenium.

When the red reduced selenium was oven-dried at 110°, it changed to the black allotrope. Precision of the analysis was then poor, but improved if air-drying was used.

Spectrophotometric analysis of the filtrate with *o*-phenylenediamine[9] showed that only 0·3 % of the selenium escaped precipitation at the 50- and 200-μg levels. Losses due to volatility or adsorption onto glassware were investigated by finding how much selenium had been precipitated. This was done by oxidizing the elemental selenium to selenious acid with fuming nitric and perchloric acids and determining this.[9] The Schöniger flask method was tried but consistently gave low (63–80 %) recoveries of selenium, and so did distillation of selenium tetrabromide (average 74 %).

An interference study was made by adding selenium to various typical metals and alloys. Table II shows that any interferences are less than the statistical error of the method (Table III), which in turn was obtained by replicate analysis of standard selenium solutions and a copper–nickel alloy. The relative standard deviation for the standard selenium sample is approximately equal to that of the copper–nickel sample, indicating no error due to matrix effects. The relative standard deviation of 1·1 % for a single sample shows that a 10-sec counting period is adequate. The precision (95 % confidence limits) is 7 μg of selenium at the 60-μg level in a copper–nickel sample.

A limit of detection was calculated, taking as the minimum a line intensity 3 standard deviations (*s*) above the background. The intensity was 27 cps per μg of

TABLE II.—DETERMINATION OF SELENIUM ADDED TO VARIOUS METALS AND ALLOYS

Material	Sample, *g*	Identification	Added	Found
Copper, 99·9%	1	J. T. Baker, 1720, CP granular	50	46
Copper, 99·9%	2	J. T. Baker, 1720, CP granular	100	105
Cu-77–Zn-20–A-12 alloy	1	NBS 1119	100	103
Nickel, 99·9%	1	Inco nickel powder	50	47
Nickel, 99·9%	2	Inco nickel powder	50	51
Ni-64–Cu-34	1	NBS 162a	100	81
Ni-64–Cr-17	1	NBS 161	100	107
Nickel base alloy	1	Ni-200	100	99
Ni-77–Cr-15–Fe-8 alloy	1	Inco NX 1476	100	109
Iron, 96%	0·2	J. T. Baker, 2226 reagent powder	40	46
Iron, 96%	0·4	J. T. Baker, 2226 reagent powder	40	39
Iron, 96%	2	J. T. Baker, 2226 reagent powder	40	39
Ingot iron	1	NBS 55e	100	86
BOH steel	1	NBS 152a	100	95

TABLE III.—PRECISION OF THE METHOD AT THE 60-μg LEVEL

	Relative std. devn., %
Replicate counts of one sample (not removed from X-ray sample holder)	1·1
Replicate counts of one sample (repositioned in sample holder)	4·1
Replicate counts of ten different samples	6·0
BCS 180/1 copper–nickel alloy	5·7

TABLE IV.—ACCURACY OF THE METHOD

Material	Identification	Selenium, *ppm* Outside lab.	X-ray	Colour
Copper (Kennecott)	1046C73	179	170	176
Copper (Kennecott)	1046D49	650	626	619
Copper shot	05235	~17	5	4
Copper cathode	05399	~3	4	3
Nickel (high purity)	04908	<0·08	0·06	—
Nickel pellets	05288	~2	0·2	0·5
Nickel squares	05365	~2	3	1
Nickel carbonyl powder	03858	~3	1	—
Copper-nickel shot	04782	~5	12	5
Ni–Cu alloy K500	HF 0460	—	1	0·8
Ni–Cu alloy 400	NBS 162a	—	1	2
Cu–Ni alloy	BCS 180/1	60	60	63
Steel	NBS 339	2470	2470	—

selenium and 525 cps for the background, and 3*s* corresponds to 69 cps or 2·5 μg of selenium—the minimum quantity detectable. The precision of the measurement at this level is 45% of the amount present, or 1·2 μg.

Only two samples, a British Chemical Standard copper–nickel alloy and an NBS steel were available as selenium reference samples. These and other samples were analysed by the spectrophotometric and X-ray methods in order to obtain an indication of the accuracy. Table IV shows that the method is applicable to both low and high concentrations of selenium in copper, iron, nickel and their alloys.

Zusammenfassung—Eine Methode zur Bestimmung von Selen in verschiedenen Metallen und Legierungen bei Konzentrationen von 3 bis 100 ppm wird beschrieben· Durch Abfiltrieren nach Reduktion der selenigen Säure zu elementarem Selen mit Hydroxylamin wird eine chemische Trennung vorgenommen. Das reine Selen läßt sich leicht durch Röntgenfluoreszenz analysieren; diese Methode ist frei von Fehlern, die durch die Hauptbestandteile bedingt sind. Für eine Kupfer-Nickel-Legierung mit etwa 60 ppm Selen beträgt die relative Standardabweichung 6%.

Résumé—On décrit une méthode pour le dosage du sélénium dans divers métaux et alliages à des concentrations de 3–100 ppm. On effectue une séparation chimique par filtration après réduction de l'acide sélénieux en sélénium élémentaire par le chlorhydrate d'hydroxylamine. Le sélénium pur produit est aisément analysé par fluorescence de rayons X; la méthode est exempte d'erreurs dues aux effets de matrice. L'écart type relatif est de 6% pour un alliage cuivre-nickel à la teneur de 60 ppm.

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GERMANOMOLYBDIC ACID AND ITS REACTION WITH BASIC ORGANIC DYESTUFFS—I

SPECTROPHOTOMETRIC DETERMINATION OF Ge(IV) WITH XANTHENE DYES

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Summary—The interaction between germanomolybdic acid and four xanthene dyes (Rhodamine B, Rhodamine 6G, Rhodamine S and Pyronine G) is studied and the conditions for spectrophotometric determination of Ge(IV) with these reagents are established.

GERMANOMOLYBDIC ACID, $H_4GeMo_{12}O_{40}$, was obtained and studied for the first time by Schwarz and Giese[1] and by Grosscup,[2] who noticed its yellow colour and recommended it for colorimetric studies, but Alimarin and Ivanov-Emin[3] were the first to develop this colorimetric method. Others[4–15] described various working conditions for the colorimetric determination of germanium by the so-called "molybdenum yellow" method. Even more numerous are the colorimetric methods based on reduction of germanomolybdic acid to blue compounds, the "molybdenum blue" method.

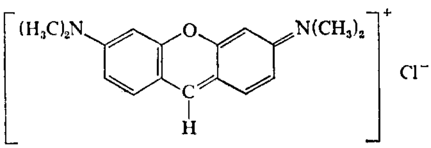
According to the literature, germanomolybdic acid can be extracted from acidic aqueous solutions by some organic solvents. Wadelin and Mellon[16] demonstrated that it can be rather well extracted by 1-butanol, 2-butanol, 2-methylpropanol, amyl acetate and ethyl acetoacetate. Shakhova and Motorkina[17] extracted it with isoamyl alcohol. Others[18,19] suggest using n-butanol in the separation of the heteropoly acids (phosphomolybdic, arsenomolybdic, germanomolybdic and silicomolybdic) by selective extraction with organic solvents at specified pH values. Paul[20] used iso-octyl alcohol, and n-butyl acetate was used by Chong Hun Won.[21]

Most authors suggest the pH range 0·9–3·4 for germanomolybdic acid formation but once formed it does not decompose even in $3{\cdot}3M$ sulphuric acid.[22]

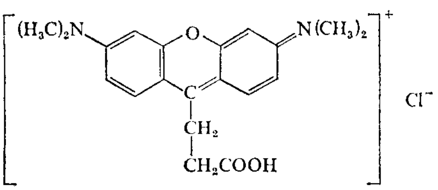
Other papers report various procedures for identifying or determining germanium by reaction of germanomolybdic acid with pyridine,[23–26] acridine,[27] cinchonine,[23,28] quinoline,[25,29,30] 8-hydroxyquinoline and its derivatives,[26,31–36] urotropine,[34] guanidine,[2,25] dimethyldiamide of pyrazoline-3,4-dicarboxylic acid,[37] and tetraphenylarsonium ions.[38]

The present paper reports the interaction of germanomolybdic acid with the following xanthene dyes: Pyronine G, Rhodamine S, Rhodamine 6G and Rhodamine B. Procedures for the spectrophotometric determination of germanium are also described.

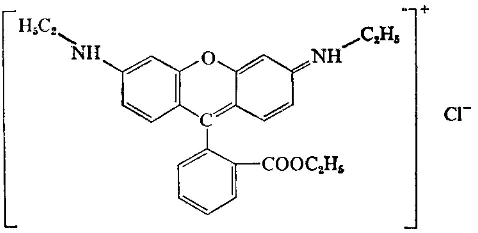
In order to find the best working conditions, we studied both the interaction between germanomolybdic acid and the dyes mentioned, and the interaction between ammonium molybdate and these dyes. It was found that the products were similar, and sparingly soluble in water, but the germanomolybdate compounds were stable



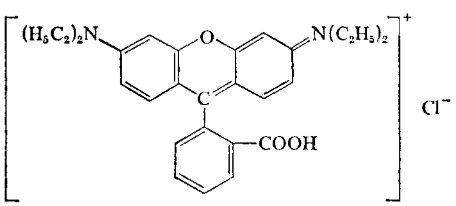
Pyronine G



Rhodamine S



Rhodamine 6G



Rhodamine B

in media as acidic as 0·7–4·5M hydrochloric acid, whereas the isopolymolybdate compounds were not. We also studied the conditions for selective extraction of both the molybdic and germanomolybdic compounds. Both behave similarly, and the germanomolybdic compounds are not extracted by the usual organic solvents such as benzene, isobutyl methyl ketone, cyclohexane, ethyl acetoacetate, n-butanol, ethyl ether, butyl ether, acetophenone, methyl n-propyl ketone, isopropyl alcohol, carbon tetrachloride, chloroform, amyl alcohol and isoamyl alcohol.

Spectrophotometric studies of the use of the four dyestuffs were limited because the Lambert-Beer law was only obeyed if the ammonium molybdate in excess was removed from the system. This was achieved by forming the germanomolybdic acid and then extracting it from 0·1–0·45N sulphuric acid medium with a 1:3 mixture of n-butanol and diethyl ether, the isopolymolybdate species remaining almost completely in the aqueous phase. The organic phase was stripped with water, and the resulting aqueous solution of germanomolybdic acid was treated with dyestuffs after adjustment to the optimum acidity. The resulting germanomolybdate–organic compounds were very sparingly water-soluble, and at sufficiently low concentration gave clear colloidal systems in the presence of gelatine, and these were further studied by spectrophotometric methods.

EXPERIMENTAL

Reagents

Germanium solution, 22 μg/ml. Prepared from germanium dioxide.
Ammonium molybdate. A 0·5% solution in 0·5M sulphuric acid.
Dyestuffs. Solutions, 10^{-2}–$10^{-4}M$, in 6M hydrochloric acid.
Gelatine. Freshly prepared 1% solution.

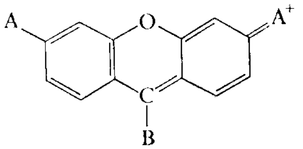
Procedure

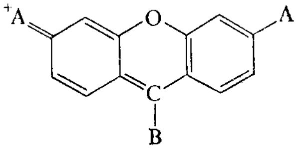
Various volumes of germanium solution (22 μg/ml) were mixed in 100-ml separating funnels with 1 ml of 0·5% ammonium molybdate solution in 0·5N sulphuric acid. A control sample was taken, containing only the ammonium molybdate solution and some water. The volume of the aqueous phase did not exceed 7·5 ml. Then 15 ml of n-butanol–ether (1:3) mixture were added and each mixture was shaken for 1 min, and left for several minutes to allow the phases to separate. The aqueous phase was removed and extracted again, first with 10 and then 5 ml of solvent mixture. The extracts were combined and stripped with first 4 and then 2 ml of distilled water; the aqueous extracts were combined in a 50-ml standard flask, treated with 2·5 ml of 1% gelatine solution (freshly prepared) and mixed well, and then a known volume of dyestuff solution was added to this heterogeneous system (8 ml of $10^{-3}M$ Rhodamine B, 12·5 ml of $10^{-3}M$ Rhodamine 6G, 10 ml of $3 \times 10^{-3}M$ Rhodamine S, or 5 ml of $10^{-3}M$ Pyronine G, all in $6M$ hydrochloric acid). The Rhodamine B solutions were diluted to volume with distilled water and the absorbance was read at $\lambda_{max} = 575$ nm, against the control, in 10-mm cuvettes. To the other solutions were added 11·5 ml of concentrated hydrochloric acid for Rhodamine 6G, 12 ml for Rhodamine S, and 14 ml for Pyronine G, then all were diluted to the mark with distilled water and mixed, and the absorbances read at λ_{max} 542–548 nm against the appropriate control, in 10-mm cuvettes.

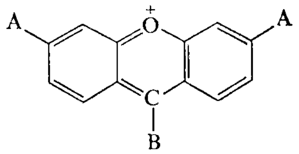
RESULTS AND DISCUSSION

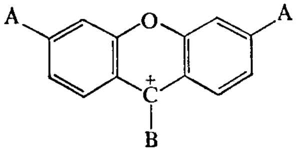
It was demonstrated that the absorption spectra of the xanthene dyestuffs are dependent on several factors, including pH, concentration, temperature, *etc.* Figure 1 shows the absorption spectra of the four dyestuffs used. The absorption spectra of the germanomolybdate-dyestuff compounds are shown in Fig. 2.

The dyestuff radicals with a xanthene nucleus may be regarded as resonance hybrids of the following canonical forms:



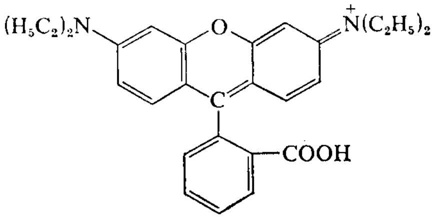






The most important results of the studies reported above are summarized in Table I. Careful study of the results suggests that Rhodamine B behaves rather differently from the other dyestuffs used, probably because of the presence of the benzoic acid group on the xanthene nucleus, which results, according to Ramette and Sandell,[39] in the occurrence of a zwitterion R^{+-}.

On acidification, the xanthene dyestuffs become protonated, resulting in the occurrence of various radicals with one or more positive charges and having a characteristic absorption maximum. In our opinion, Rhodamine B has a different protonation scheme, since the zwitterion R^{+-} is able to accept a proton without difficulty



and to form the RH^+ radical which has a red-violet colour and an absorption maximum at 556 nm. This radical may exist only between certain acidity limits. On further acidification protons begin to add on to one of the A groups, forming the RH_2^{2+}

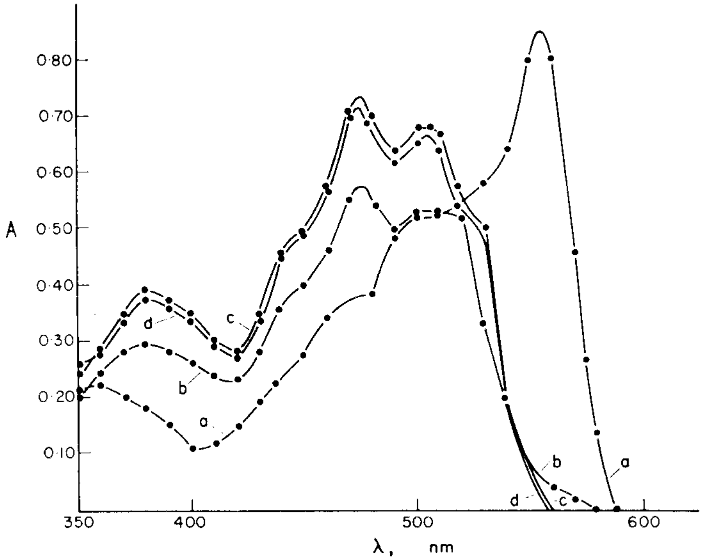


FIG. 1.—Absorption spectra of xanthene dyes: (*a*) Rhodamine B, (*b*) Rhodamine 6G, (*c*) Rhodamine S, (*d*) Pyronine G.

Final conditions (*a*) 1*M* HCl, 0·05% gelatine, $1·6 \times 10^{-4}M$ Rhodamine B. (*b*) 4*M* HCl, 0·05% gelatine, $1·2 \times 10^{-4}M$ Rhodamine 6G (*c*) 4*M* HCl, 0·05% gelatine, $3 \times 10^{-4}M$ Rhodamine S (*d*) 4*M* HCl, 0·05% gelatine, $5 \times 10^{-5}M$ Pyronine G. Water as reference; 10-mm cuvettes.

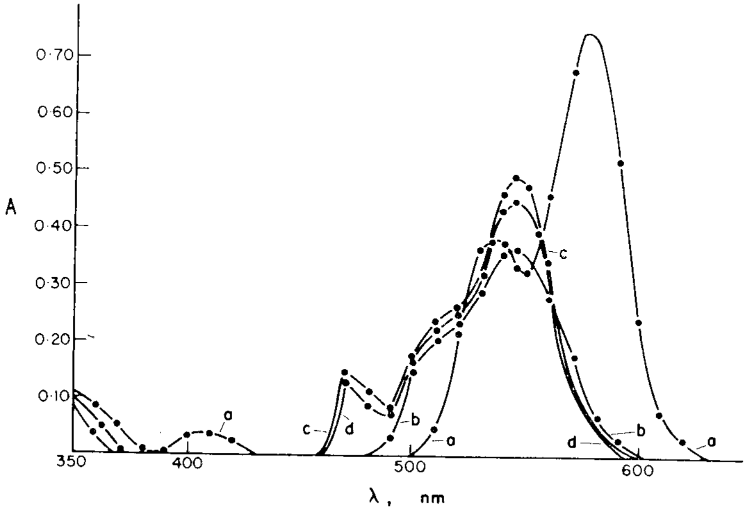


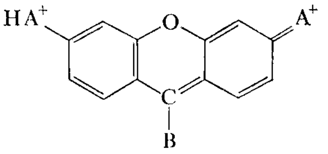
FIG. 2.—Absorption spectra of germanomolybdate–dyestuff compounds: (*a*) Rhodamine B, (*b*) Rhodamine 6G, (*c*) Rhodamine S, (*d*) Pyronine G. Conditions described in text.

TABLE I

Dyestuff	A	B	Weight of the basic dyestuff cation	Solution acidity, [HCl], *M*	λ_{max}, *nm*		Lembert-Beer law range, μg	Molar absorptivity, *l.-mole*$^{-1}$*.cm*^{2}
					Dyestuff	Compounds		
Pyronine G	$N(CH_3)_2$	H	267	3·75–4·5	472–474 (473)	542–546 (544)	0·05–0·85	6·6 × 10^4
Rhodamine S	$N(CH_3)_2$	C_2H_4COOH	339	3·75–4·5	472–475 (474)	544–546 (545)	0·045–0·70	8·2 × 10^4
Rhodamine 6G	$NH(C_2H_5)$	$C_6H_4COOC_2H_5$	416	3·75–4·5	474–476 (475)	544–548 (546)	0·04–0·65	9·1 × 10^4
Rhodamine B	$N(C_2H_5)_2$	C_6H_4COOH	444	0·75–1·5	556	576	0·03–0·45	1·34 × 10^5

radical (orange), but the occurrence of the RH_3^{3+} state (yellow) is possible only in very acid solutions.

On the other hand, it appears that in Pyronine G, Rhodamine S and Rhodamine 6G the protonation starts by proton addition to one of the A groups, resulting in radicals such as



which have a colour obviously distinct from that of the original R^+ since the added proton blocks the resonance and therefore the compound becomes orange. In very acid solutions of Pyronine G, Rhodamine S and Rhodamine 6G, the occurrence of the RH_2^{3+} radical (yellow) is also possible. Although Rhodamine S has, like Rhodamine B, a non-esterified carboxyl group, there is a clear distinction between their behaviour, probably due to the fact that this group is attached in the one instance to an aliphatic group, and the other to an aromatic.

It is also found that the higher the temperature and dyestuff concentration, the greater is the dimerization of the radicals. Hence, in different practical working conditions, a complicated set of equilibria would occur, resulting from the protonation and dimerization processes. The fact prevented us from applying the Job method for studying the stoichiometry of the compounds formed by these dyestuffs and germanomolybdic acid.

From the absorption spectra of the four dyestuffs used (Fig. 1) the following conclusions may be drawn. Rhodamine B has its absorption maximum at 556 nm and the major species would probably be the RH^+ radical; Rhodamine 6G, Rhodamine S and Pyronine G have a nearly identical absorption maximum between 472 and 478 nm and the major species may be the RH^{2+} radical, which would explain the identical behaviour of these three dyestuffs in the protonation process.

The germanomolybdate compounds of Rhodamine 6G, Rhodamine S and Pyronine G, though less sensitive than that of Rhodamine B, are particularly stable in comparatively concentrated hydrochloric acid media (3·75–4·5*M*) and should therefore provide a successful solution to the problem of interference by other ions since there are few similar compounds stable in such conditions. We inferred from some qualitative tests that these reagents are more sensitive than Rhodamine B in less acidic media, but they cannot be used in such conditions because of their strong fluorescence, which reaches its lowest level (or disappears) only when the acidity is increased to within the limits given.

Concerning the effect of the reaction medium, we should emphasize that many authors have studied germanium compounds in hydrochloric acid media, but many of their conclusions are approximate or inconsistent. We may state, however, that at hydrochloric acid concentrations of 0·1–4*M* germanium anionic complex formation is very small (or negligible),[40,41] and that Benoit and Clerc[42] point out that only at hydrochloric acid concentrations higher than 5·6*M* are the species $[GeCl_i(OH)_j(H_2O)_k]^{(i+j-4)}$ possible, but $[GeCl_6]^{2-}$ is not formed, even if the acid concentration exceeds 12*M*.

Zusammenfassung—Die Reaktion zwischen Germanomolybdänsäure und vier Xanthenfarbstoffen (Rhodamin B, Rhodamin 6G, Rhodamin S und Pyronin G) wird untersucht und die Bedingungen zur spektrophotometrischen Bestimmung von Ge(IV) mit diesen Reagentien ermittelt.

Résumé—On étudie l'interaction entre l'acide germanomolybdique et quatre colorants du xanthène (Rhodamine B, Rhodamine 6G, Rhodamine S et Pyronine G) et établit les conditions de détermination spectrophotométrique du Ge(IV) avec ces réactifs.

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COLLECTION OF TRACES OF METALS ON CARBOXY CELLULOSE CATION-EXCHANGER

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Summary—Carboxy cellulose ("C-cell") is a cation-exchanger based on cellulose and having carboxyl functional groups with pK 3·46 ± 0·05 at 20 ± 1° in $1M$ sodium chloride. The capacity of the exchanger is pH-dependent and the maximum is 0·22 mequiv/g. The capacity is also influenced by the dielectric constant of the medium and by the swelling of the cellulose. C-cell is suitable for the collection of metal ion impurities from aqueous and non-aqueous media.

HYPOBROMITE-OXIDIZED cellulose—oxycellulose or "C-cell"—functions as an ion-exchanger and is useful for collecting traces, 1–100 ng, of metal ions from 100–1000 ml of aqueous or organic solutions.[1–7] In some respects, C-cell is more effective than ion-exchange resins for the concentration of metals from extremely dilute solutions, although it has only a tenth of the capacity. Its density is lower than that of carboxy methyl cellulose—an ion-exchanger with the same functional group.[6] In this paper the ion-exchange properties of the functional group of C-cell and further applications are discussed.

EXPERIMENTAL

Reagents

C-cell (H^+ *form*). Prepared as previously described.[3] Purity checked by washing with dilute hydrochloric acid and testing the washings with dithizone. Purified if necessary, by washing with $0{\cdot}5M$ hydrochloric acid followed by purified distilled water till acid-free. Fraction used contains fibrils 0·6–0·8 mm long.[3] Converted into salt form by means of metal acetate. A 6-year old sample stored in a stoppered bottle maintained its capacity.

Purified distilled water. Passed through a column of C-cell.

Cotton wool. Free from iron—purified by method used for C-cell.

Analytical grade reagents were used throughout.

Apparatus

Ion-exchange columns. Glass tubes with inner diameter of 10, 14 or 28 mm and length 170 mm, fitted with a perforated glass disc.

Pretreatment of glassware, etc. Wash the glass or polyethylene flasks with hot concentrated nitric acid and then with purified distilled water. Shaking with a C-cell suspension in purified water will remove adsorbed metals.

Packing of the C-cell column. Place some purified cotton wool (air-dried) at the bottom of the tube. Suspend 0·20, 1·00 or 5·00 g of C-cell in purified water and pour it into the column. The C-cell will settle down, suction is unnecessary. Cover the column with a layer of cotton wool and maintain the water level above it. If a water-immiscible solvent is used instead of water, air-dried C-cell must be placed in the column.

Infrared spectra. Potassium bromide discs were used.

Procedures

Titration curve. C-cell (1 g) was suspended in $1M$ sodium chloride solution (50 ml) and titrated potentiometrically directly with $1M$ sodium hydroxide at 20 ± 1°. The solution was stirred with a slow stream of nitrogen.

Capacity measurements. (*a*) The capacity of C-cell was obtained from the volume of titrant at the inflection point of the titration curve.

(*b*) Calcium acetate solution (50 ml, 0·05*M*) was poured onto 1·000 g of C-cell. The mixture was shaken and then allowed to stand overnight. The suspension was collected on a Hirsch-filter, and the calcium in the filtrate was determined by titration with EDTA. The calcium on the C-cell was similarly determined after elution with 10 ml of hydrochloric acid.

Influence of anions on the collection of metals. Nickel acetate, chloride, nitrate, or sulphate (50 ml, 0·005*M*) was poured onto 1·000 g of C-cell. The suspension was allowed to stand overnight, then the C-cell was filtered off and the adsorbed nickel was determined titrimetrically with EDTA after elution.

Stoichiometry of the exchange. Calcium, copper or lead nitrate solution (50 ml, 0·005 or 0·05*M*) was poured onto 1·000 g of C-cell, and allowed to stand overnight. C-cell was filtered off, the metals in the filtrate were determined with EDTA, and the acid liberated was titrated with standard alkali in the presence of sodium thiosulphate.[9]

Break-through capacity. This was determined in the standard way by passing 0·05*M* solutions of zinc, nickel or copper sulphate, or lead nitrate through a column containing 5·00 g of C-cell, at a flow-rate of 3 ml/min. The metals were detected in the eluate (3-ml fractions) by Methylthymol Blue, dimethylglyoxime, rubeanic acid and dithizone respectively. Both the H and Na form of C-cell were used.

Procedures for analysis with C-cell

Qualitative and semiquantitative. Procedures for the collection of metal ions have been given.[3] The spot test procedure has proved most valuable for identification of eluted ions. We have found that the procedure of titration to equal colour,[10,11] in which equal amounts of colour-forming reagent are added to the element and a blank, and the blank is titrated with a standard solution of the metal ion until the solutions have equal colour intensity, to be the most useful for semiquantitative determination. Copper can be determined with lead diethyldithiocarbamate at the 0·1–0·5 ppm level with a precision of 10% by this procedure.[12]

Quantitative. Pack a micro-column, 10 mm in diameter, with 0·200 g of C-cell. Allow the solution to be analysed to pass through the column. If organic solvent is used, wash out the solvent from the column with metal-free ethanol before elution of the fixed metals from the C-cell. Elute the metals with dilute acid and determine them by a suitable method.

Purification of solutions or solvents. Pass the solution or solvent through a column of 14–28 mm diameter packed with 1–5 g of C-cell, at a flow-rate of 50–60 ml/min for water and 3–5 ml/min for organic solvents; 1 g of C-cell will purify 10 l. of water if the heavy metal impurities are $<10^{-5}$%.

RESULTS AND DISCUSSION

The Functional Group of Carboxy Cellulose

Carboxy cellulose is prepared by oxidation of medical cotton with sodium hypobromite solution. The bulk of the fibrils produced have the same length. Carboxyl groups are formed, and can be identified by infrared spectroscopy (Figs. 1*a* and 1*b*). C-cell contains only 1% of carboxyl groups and for this reason the absorption bands at 1630 cm^{-1} and 1740 cm^{-1}, due to the carboxylate ion and to the carbonyl group respectively, are of low intensity. Figure 1*c* shows the spectrum of a dicarboxy cellulose (DC-cell)* containing 10% carboxyl. The spectrum of DC-cell is identical with that published earlier and that of C-cell is similar to that of nitrogen dioxide-oxidized cellulose.[3] The product of the nitrogen dioxide and hypobromite oxidation is a so-called acidic oxidized cellulose, with carboxyl groups attached to the cellulose chain. The length of the nitrogen dioxide-oxidized cellulose fibres is a few cm whilst the fibres of cellulose are reduced to powder by the hypobromite oxidation. The carboxyl groups are attached directly to the cellulose chain in C-cell, whereas —CH_2COOH groups are attached to the cellulose hydroxy group in carboxy methyl cellulose (CM-cell).[14]

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* DC-cell is prepared by two-step oxidation (periodate, then chlorous acid) of cellulose.

FIG. 1.—Infrared spectra of C-cell and related substances.

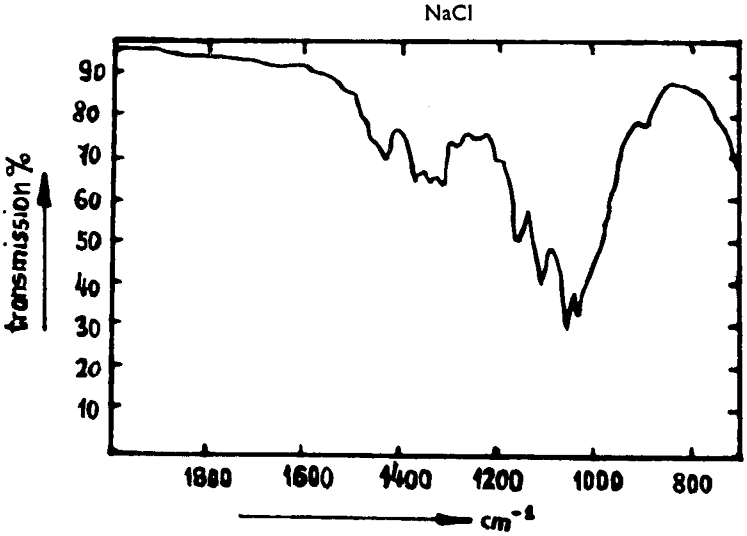

FIG. 1*a*—cellulose powder.

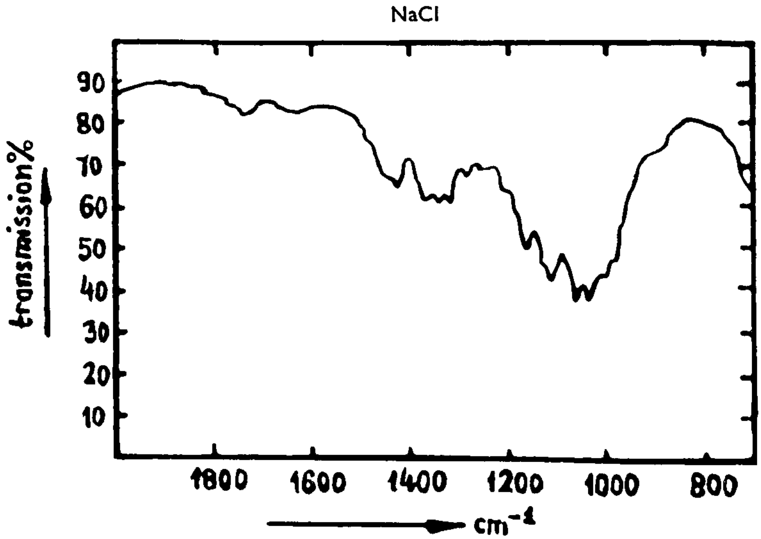

FIG. 1*b*—C-cell.

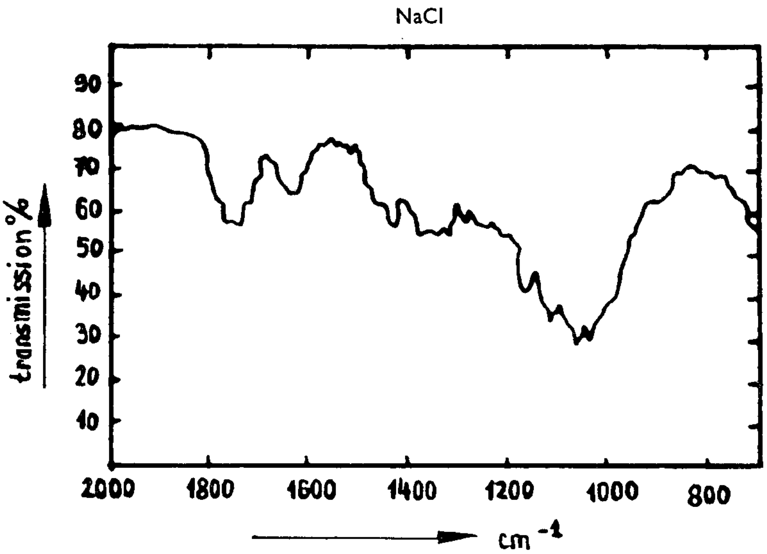

Fig. 1c—DC-cell.

All the evidence from ion-exchange experiments, titration curves and IR spectra indicates the carboxyl group as being the functional group of C-cell. The pH-dependence of the exchange capacity is characteristic of resins with carboxyl functional groups and of CM-cell. The consequence of the pH dependence is the easy elution of metal ions by dilute acids.

Exchange capacity

The titration curve was obtained by direct titration in the presence of strong electrolyte (Fig. 2). Exchange equilibrium is reached within a few min, which is much more rapidly than for exchange on carboxylic resins. The apparent dissociation constant of the functional group of carboxy cellulose was calculated in a standard manner.[15,16] At 20 ± 1° in $1M$ sodium chloride the pK is 3·46 ± 0·05, which may be compared with values for the pK of CM-cell, of 3·6[17] and 3·8.[18] The latter figure was obtained from the half-neutralization of the exchanger. The experimental conditions differed in both cases from those of ours.

The maximum exchange capacity of C-cell as determined by the titration (Fig. 2) and calcium methods is 0·22 mequiv/g. The uptake of metal ions on C-cell is pH-dependent and the maximum exchange capacity can only be reached when a weak acid is formed as a result of the hydrogen ion–metal ion exchange, *e.g.*, when the salt is an acetate. The uptake of nickel(II) (mequiv/g of C-cell) from 0·005M solution of nickel salts is 0·206 for the acetate and 0·076, 0·077, 0·068 for the chloride, nitrate and sulphate respectively.

The exchange on C-cell is stoichiometric. The break-through capacity is in good accordance with the affinity scale given earlier.[7] Metal ions appear in the effluent in the order Zn, Ni, Cu, Pb from an H or Na-form carboxy cellulose column.

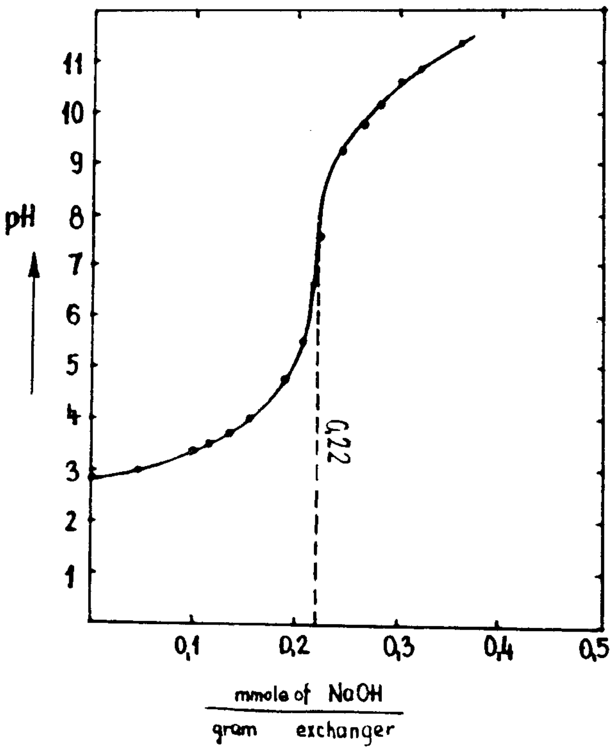

FIG. 2.—Titration curve of C-cell.

The Uptake of Metals from Solvents

C-cell collects metal ions from organic solvents.[4] The earlier work has been extended and some of the results are given in Table I. Copper(II) (10 μg in 100 ml of solvent) was passed through a micro-column and the copper subsequently eluted with 3 ml of 5% hydrochloric acid and determined. The recovery was 10 ± 3 μg from water, methanol, ethanol, propanol, acetone, dioxan and benzene. The comparison of the quantity of metals fixed at 0·05 mole fraction of water, the dielectric constant of the solvent and the swelling of the cellulose in the particular solvent,[2,19] shows that the uptake depends on the cellulose-solvent interaction. Under similar

TABLE I.—UPTAKE OF 10 μg OF LEAD FROM WATER–SOLVENT MIXTURES

Solvent	Mole fraction of water in solution						Dielectric constant	Swelling, %
	0·00	0·05	0·2	0·5	0·8	0·95		
Dimethyl-formamide	3·4	3·4	4·8	5·7	5·8	8·0	37	
Methanol	2·8	2·8	4·2	5·2	5·8	8·3	32	95
Ethanol	2·2	2·2	2·2	4·3	6·0	7·8	24	83
Acetone	2·0	2·0	3·4	—	4·8	7·6	21	63
n-Propanol	0·9	0·9	1·0	4·8	5·2	5·2	20	45
n-Butanol	0·8	0·8	3·2	—	—	—	18	13·5
Dioxan		—	—	2·3	5·2	5·2		

Results expressed as μg. Uptake from water, 8·3 μg; dielectric constant, 78; swelling, 100%.

conditions, the uptake of metal increases with increase in dielectric constant and the degree of swelling of the cellulose.

Ion-exchange processes in organic solvents have not been so extensively studied as those in aqueous solutions, especially on ion-exchange celluloses. The differences in the exchange rate in different solvents should also be taken into consideration. Experiments in this direction are in progress.

The application of C-cell

Traces of metals at the 0·001–0·1 ppm level can be collected on 1–5 g of C-cell from 100–1000 ml of solution. The impurity level is generally lowered to 10^{-7}%. For the collection of alkaline earth metals and heavy metals the best pH range is 3–10 and for the rare earth metals, 3–4.

The collection of the following metal ions has been studied: Ag(I), Al(III), Ba(II), Bi(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Hg(II), In(III), La(III), Mn(II), Ni(II), Pb(II), Pr(III), Ru(II), Sr(II), UO_2(II), VO(IV), Y(III), Zn(II). The common metallic impurities in water, solutions of sodium and ammonium chlorides, sulphates and acetates, distilled ethanol and methanol, carbon tetrachloride and trichloroethylene have been reduced from 10^{-4}% to 10^{-7}%.[20] The removal of trace amounts of radioactive isotopes from reactor-cooler water has been investigated.[21]

Acknowledgements—The authors wish to thank Dr. F. Ruff for his help in evaluating the infrared spectra.

Zusammenfassung—Carboxycellulose ("C-cell") ist ein Kationenaustauscher auf Cellulosebasis mit Carboxylgruppen, die bei 20 ± 1° einen pH von 3,46 ± 0,05 in 1*M* Natriumchlorid aufweisen. Die Kapazität des Austauschers hängt vom pH ab und beträgt maximal 0,22 mäq/g. Die Kapazität wird auch durch die Dielektrizitätskonstante des Mediums und den Quellungszustand der Cellulose beeinflußt. C-cell ist geeignet zur Aufnahme von Verunreinigungen durch Metallionen aus wäßrigen und nichtwäßrigen Medien.

Résumé—La carboxy cellulose ("C-cell") est un échangeur de cations fondé sur la cellulose et ayant des groupes fonctionnels carboxyle avec un pH de 3,46 ± 0,05 à 20 ± 1° en chlorure de sodium 1 *M*. La capacité de l'échangeur dépend du pH et le maximum est de 0,22 méquiv/g. La capacité est également influencée par la constante diélectrique du milieu et par le gonflement de la cellulose. La C-cell convient pour recueillir les impuretés à l'état d'ions métalliques de milieux aqueux et non aqueux.

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ELEMENTS DE FLUORIMETRIE ORGANIQUE FONCTIONNELLE—II

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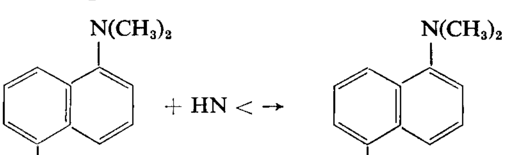
Résumé—On condense les acides α-aminés en dérivés fluorescents de la dihydrolutidine. Les alcoylamines primaires et secondaires sont dosables par formation de sulfonamides au moyen du chlorure de dansyle. Les alcoylamines tertiaires fournissent un condensat fluorescent avec l'acide α,γ-anhydroaconitique en anhydride acétique, et les indoles développent une fluorescence par action du formol en présence d'oxydant. Le furfural obtenu par déshydratation des pentoses est dosable par formation d'un dérivé de la 1,8-dioxo décahydroacridine. Le 2,6-di*ter*butyl *p*-crésol permet la fluorimétrie des Δ^{4} et $\Delta^{1,4}$ 3,11-dicétostéroïdes. La fluorescence de la pyronine G décroît sous l'action des $\Delta^{5(10)}$ 3-céto 19-nor stéroïdes.

DE NOUVEAUX dosages fonctionnels par fluorimétrie ont été mis au point suivant les principes précédemment décrits.[1]

La réaction des alcoylamines primaires avec l'acétylacétone et le formaldéhyde peut, avec de légères modifications dans le mode opératoire, être également appliquée à la fluorimétrie des acides α-aminés et la technique ici proposée est plus simple que celle de Sawicki et Carnes.[2]

La condensation des amines et acides α-aminés sur le chlorure de l'acide 1-diméthylamino naphtalène 5-sulfonique (chlorure de dansyle) fournit des sulfonamides fluorescents, dont la formation a été mise à profit pour détecter les protéines, puis les acides α-aminés et les amines sur chromatogrammes[3–6] et éventuellement les doser après élution.[6] Sur ce principe, en milieu non aqueux, on peut effectuer la fluorimétrie des alcoylamines primaires et secondaires.



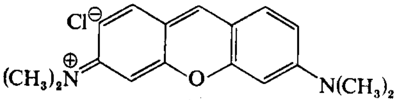
Groth et Dahlen[7] ont décrit une réaction d'identification des amines tertiaires par développement d'une coloration violette à l'aide de l'acide α,γ-anhydroaconitique en anhydride acétique. Ce réactif préparé *in situ* fournit également, dans des conditions convenables, une fluorescence verte avec les alcoylamines tertiaires.

La fluorescence que développent les dérivés indoliques en présence de formol,[8] exaltée par une trace d'oxydant, peut être rendue quantitative.

La fonction aldéhyde du furfural obtenu par déshydratation des pentoses en milieu chlorhydrique est révélée par la 1,3-cyclohexanedione en présence d'ammoniac.[1]

Les 3-cétostéroïdes, sous l'action du 2,6-di*ter*butyl *p*-crésol en milieu alcalin et en présence d'eau oxygénée, développent des colorations diverses.[9] A de plus faibles concentrations, les Δ^4 et $\Delta^{1,4}$ 3,11-dicétostéroïdes fournissent également une fluorescence.

L'enchaînement β,γ-éthylénique des $\Delta^{5(10)}$ 3-céto 19-nor stéroïdes favorise le virage en milieu alcalin des colorations de la thionine et du bleu de méthylène.[10] La pyronine G (I) offre une structure comparable à celles de ces deux colorants, et sa fluorescence décroît en présence des mêmes stéroïdes.



(I)

PARTIE EXPERIMENTALE*

La sensibilité est exprimée selon les conventions antérieurement précisées.[1]

Acides α-aminés

Principe. Formation de dihydrolutidines N-substituées par condensation sur l'acétylacétone et le formaldéhyde: fluorescence jaune-vert.

Réactif. A 10 ml de solution aqueuse *M* d'acétate de sodium, on ajoute extemporanément 0,4 ml d'acétylacétone et 1 ml de solution aqueuse à 30% de formaldéhyde. On dilue à 30 ml par l'eau.

Mode opératoire. A 1 ml de solution aqueuse d'acide α-aminé, on ajoute 1 ml de réactif, bouche les tubes par un tampon de coton, chauffe pendant 10 mn au bain-marie bouillant à l'abri de la lumière vive, refroidit dans un bain eau-glace et ajoute 2 ml d'eau. Lecture à l'excitation 405 nm.

Etalon. Solution de 2-méthyl 5-carboxy 7-amino quinoléine dans l'acide acétique pur.

Applications. Voir Tableau I.

TABLEAU I

	λ d'émission, *nm*	Limites du dosage, *μg*	Lecture 50	
			Essai, *μg*	Etalon, *μg/ml*
Glycocolle	485	2–10	4,5	0,042
Phénylalanine	490	8–40	17,2	0,044
Sérine	485	5–25	10	0,032
Cystéine (chlorhydrate)	500	20–100	38	0,040
Acide glutamique	485	20–100	43	0,035

Alcoylamines primaires et secondaires

Principe. Formation de sulfonamides par réaction avec le chlorure de l'acide 1-diméthylamino naphtalène 5-sulfonique: fluorescence jaune-vert.

Réactifs. (*a*) Solution alcoolique 0,01*N* de potasse, diluée au 1/25 par l'acétonitrile. (*b*) Solution à 0,05% (p/v) de chlorure de dansyle dans l'acétone.

Mode opératoire. A 1 ml de solution d'amine dans l'acétonitrile, on ajoute 0,2 ml de réactif *a* puis 0,2 ml de réactif *b*. On agite puis laisse reposer pendant 5 mn à l'obscurité à température ordinaire, avant d'ajouter 3 ml d'acétone. Lecture à l'excitation 366 nm, émission 510 nm.

Etalon. Solution de 3,5-diacétyl 1,4-dihydrolutidine dans l'éthanol-eau 1:1.

Applications. Voir Tableau II.

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* Avec M^me^ P. Balleydier, M^me^ C. Colombat et M^elle^ M. Pépin.

TABLEAU II

	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
Ethylamine	0,3–1,5	0,69	6,15
n-Propylamine	0,4–2,0	0,9	6,35
n-Butylamine	0,4–2,0	0,86	5,5
Benzylamine	1,0–5,0	2,05	6,05
Diéthylamine	1,0–5,0	2,3	6,2
Di-*n*-propylamine	1,2–6,0	2,7	6,35
Di-*n*-butylamine	1,2–6,0	2,6	5,45
Dibenzylamine	50–250	95	4,5

Remarque. La réaction est pratiquement négative pour les arylamines primaires et secondaires pour des prises d'essai inférieures à 200 μg.

Alcoylamines tertiaires

Principe. Le réactif obtenu à partir du mélange acide aconitique-anhydride acétique développe avec les alcoylamines tertiaires une fluorescence verte.

Réactif. On dissout 0,25 g d'acide aconitique dans 2,5 ml d'acétone, ajoute 1 ml d'anhydride acétique et laisse reposer pendant 20 mn à 40°. On laisse refroidir, ajoute 40 ml de chlorure de méthylène, agite, laisse reposer pendant 5 mn dans un bain eau-glace puis filtre. Le filtrat est dilué à 50 ml par le chlorure de méthylène. Ce réactif est stable pendant plusieurs heures à température ordinaire.

Mode opératoire. A 4 ml de solution d'amine dans l'acétate d'éthyle on ajoute, à l'abri de la lumière, 0,2 ml de réactif. Lecture avant 5 mn à l'excitation 405 nm, émission 485 nm.

Etalon. Solution de 2-méthyl 5-carboxy 7-amino quinoléine dans l'acide acétique.

Applications. Voir Tableau III.

TABLEAU III

	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
Triéthylamine	1–5	2,3	0,029
Tri-*n*-propylamine	2–10	4,5	0,027
Tri-*n*-butylamine	2–10	4,4	0,024

Remarques. L'acide aconitique utilisé doit être parfaitement blanc. On le recristallise au besoin en acide acétique. La fluorescence est stable pendant 5 mn environ à condition de maintenir les tubes à l'obscurité. Les lectures doivent être effectuées rapidement, la fluorescence étant progressivement détruite par la lumière excitatrice. La sensibilité est un peu plus élevée si l'on opère à 0°, mais les amines secondaires fournissent alors une fluorescence assez stable, dont la fugacité à température ordinaire ne gêne pas le dosage des amines tertiaires. La réaction est négative avec la N,N-diméthylaniline.

Dérivés indoliques

Principe. Condensation en milieu acide sur le formaldéhyde en présence d'eau oxygénée: fluorescence jaune à jaune-orangé.

Réactifs. (*a*) Solution aqueuse à 0,0005 volume d'eau oxygénée. (*b*) Solution aqueuse à 3% de formaldéhyde obtenue en diluant au dixième la solution commerciale à 30%.

Mode opératoire. A 0,5 ml de solution de dérivé indolique dans un mélange à parties égales d'éthanol et d'acide acétique on ajoute 0,1 ml de réactif *a*, 0,1 ml de réactif *b* et 0,6 ml d'acide perchlorique à 65% (d = 1,615). On bouche les tubes par un tampon de coton et, après 1 h de repos à 60° à l'abri de la lumière, on refroidit pendant 2 mn dans un bain eau-glace puis ajoute 4 ml d'acide acétique pur.

Etalon. Solution de 3,5-diacétyl 1,4-dihydrolutidine dans l'eau à 2% d'éthanol.

Applications. Voir Tableau IV.

TABLEAU IV

	λ d'excitation, *nm*	λ d'émission, *nm*	Limites du dosage, *μg*	Lecture 50	
				Essai, *μg*	Etalon, *μg/ml*
Tryptophane	436	540	1–5	2,3	0,76
N-Acétyl tryptophane	436	540	2–10	4,7	1,19
Acide 3-indole acétique	436	540	2–10	4,8	2,63
Tryptamine	436	540	1–5	2,3	0,74
Acide 3-indole carboxylique*	366	490	0,5–2,5	1,2	0,09

* L'étalon est une solution de sulfate de quinine dans l'acide sulfurique 0,1*N*.

Remarque. La réaction n'est pas applicable à l'indole lui-même, ni à ceux des dérivés indoliques dont la fluorescence spontanée en solution est intense.

Pentoses

Principe. Chauffage en milieu acide pour former du furfural que l'on révèle par la 1,3-cyclohexanedione et l'ammoniac: fluorescence jaune-vert.

Réactifs. (*a*) Solution tampon obtenue en dissolvant 10 g d'acétate de sodium anhydre et 10 ml d'acide acétique dans l'eau, q.s.p. 50 ml. (*b*) Solution à 0,25% (p/v) de 1,3-cyclohexanedione dans la solution aqueuse à 40% (p/v) d'acétate d'ammonium, fraîchement préparée.

Mode opératoire. A 1 ml de solution aqueuse de pentose, on ajoute 1 ml d'acide chlorhydrique concentré et chauffe pendant 1 h au bain-marie bouillant, les tubes étant surmontés de réfrigérants à air. Après refroidissement, on ajoute 1 ml de lessive de soude 10*M* puis continue l'addition goutte à goutte jusqu'à réaction alcaline à la touche de la phénolphtaléine. On introduit ensuite 1 ml de solution tampon *a* et 1 ml de réactif *b* et chauffe pendant 30 mn à 60°. On refroidit à 0° dans un bain eau-glace et ajoute 2,5 ml de lessive de soude 10*M*. Lecture immédiate à l'excitation 436 nm, émission 495 nm.

Etalon. Solution de 2-méthyl 5-carboxy 7-amino quinoléine dans l'acide acétique.

Applications. Voir Tableau V.

TABLEAU V

	Limites du dosage, *μg*	Lecture 50	
		Essai, *μg*	Etalon, *μg/ml*
Arabinose	0,8–4,0	1,5	0,31
Ribose	0,5–2,5	1,0	0,40
Xylose	0,5–2,5	0,9	0,36
Lyxose	0,5–2,5	1,0	0,36

Remarque. Les aldohexoses sont beaucoup moins réactifs. Ainsi, le dosage n'est possible qu'entre 20 et 100 μg pour le glucose et le galactose, 50 et 500 μg pour le fructose avec lequel la loi de linéarité n'est pas suivie.

Δ^4 *et* $\Delta^{1,4}$ 3,11-*dicétostéroïdes*

Principe. Action du 2,6-di*ter*butyl *p*-crésol en milieu alcalin et en présence d'eau oxygénée. La fluorescence, pratiquement invisible sous la lumière d'une lampe de Wood, n'est décelée qu'au fluorimètre.

Réactifs. (*a*) Solution alcoolique à 1% (p/v) de 2,6-di*ter*butyl *p*-crésol. (*b*) Solution aqueuse à 0,1 volume d'eau oxygénée.

Mode opératoire. A 2 ml de solution de cétostéroïde dans l'éthanol, on ajoute 1 ml de réactif *a*, 0,2 ml de réactif *b* et 2 ml de solution *N* de soude. On chauffe pendant 30 mn à 80° sous lumière douce et laisse refroidir pendant 2 mn dans un bain eau-glace. Lecture à l'excitation 436 nm, émission 520 nm.

Etalon. Solution de 3,5-diacétyl 1,4-dihydrolutidine dans l'éthanol à 50% d'eau.
Applications. Voir Tableau VI.

TABLEAU VI

	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
Adrénostérone	1–5	1,8	0,159
Cortisone	1–5	2	0,175
Pregnisone	40–200	82	0,185

Remarque. La réaction est également positive avec l'acide déhydrocholique, avec l'excitation 405 nm, émission 485 nm, le dosage étant effectué entre 4 et 20 μg.

$\Delta^{5(10)}$ *3-céto 19-nor stéroïdes*

Principe. L'enchaînement cétone β,γ-éthylénique favorise, en milieu alcalin, la disparition de fluorescence de la pyronine G.

Réactif. Solution aqueuse à 0,001% de pyronine G.

Mode opératoire. Toutes les manipulations sont effectuées à l'abri de la lumière, dans un bain eau-glace. A 1 ml de solution méthanolique d'un cétostéroïde, on ajoute 1 ml de réactif, 2,5 ml d'eau et 0,2 ml de solution *N* de soude. On agite laisse reposer pendant 3 mn et ajoute 0,15 ml d'acide acétique. On agite et effectue immédiatement la lecture à l'excitation 546 nm, émission 570 nm.

Etalon. Cette réaction fait appel à une fluorimétrie par décroissance. L'étalon est constitué par le témoin des réactifs, pour lequel le fluorimètre est réglé à la lecture 100.

Applications. Voir Tableau VII.

TABLEAU VII

	Limites du dosage, μg	Lecture pour la prise d'essai la plus forte
3-Oxo 19-nor 5(10)-prégnène 20-one	1–4	45
3-Oxo 17β-hydroxy 5(10)-estrène	0,5–2,5	40
3-Oxo 17α-éthyl 17β-hydroxy 5(10)-estrène	0,6–3,0	46
3-Oxo 17α-éthinyl 17β-hydroxy 5(10)-estrène	0,5–2,5	36
3-Oxo 17β-hydroxy 5(10), 9(11)-estradiène (benzoate)	1–4	40

Remarque. La pyronine G est très fortement adsorbée par le verre des cuves de lecture. Entre deux séries de mesures, celles-ci doivent être lavées à l'acide sulfurique concentré.

Summary—α-Amino acids are converted into fluorescent derivatives of dihydrolutidine. Primary and secondary alkylamines are determined by converting them into sulphonamides by means of 1-dimethylaminonaphthalene-5-sulphonyl chloride. A fluorescent adduct is given by the reaction of tertiary alkylamines with α,γ-anhydroaconitic acid in acetic anhydride, and a fluorescence is obtained by condensing indoles with formaldehyde in the presence of an oxidizing agent. Furfural, obtained by the dehydration of pentoses, is determined by converting it into a 1,8-dioxodecahydroacridine derivative. 2,6-Di-t-butyl-*p*-cresol allows the fluorimetry of Δ^4 and $\Delta^{1,4}$-3,11-diketosteroids. The fluorescence of Pyronine G decreases under the action of $\Delta^{5(10)}$-3-keto-19-norsteroids.

Zusammenfassung—α-Aminosäuren werden in fluoreszenzfähige Dihydrolutidinderivate überführt. Primäre und sekundäre Alkylamine werden durch Umsetzung mit 1-Dimethylaminonaphthalin-5-sulfonsäurechlorid zu Sulfonamiden bestimmt. Die Reaktion tertiärer Alkylamine mit α,γ-Anhydroaconitsäure in Acetanhydrid liefert ein fluoreszierendes Addukt; auch durch die Kondensation von Indolen mit Formaldehyd in Gegenwart eines Oxidationsmittels erhält man Fluoreszenz. Aus der Dehydratisierung von Pentosen stammendes Furfural wird durch Überführung in ein 1,8-Dioxodekahydroacridinderivat bestimmt. 2,6-Di-*t*-butyl-*p*-kresol erlaubt die fluorimetrische Bestimmung von Δ^4- und $\Delta^{1,4}$-3, 11-Diketosteroiden. Die Fluoreszenz von Pyronin G nimmt in Gegenwart von $\Delta^{5(10)}$-3-Keto-19-norsteroiden ab.

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RADIOCHEMICAL MICRODETERMINATION OF MANGANESE, STRONTIUM AND BARIUM BY ION-EXCHANGE

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Summary—A rapid radiochemical ion-exchange method has been developed for the quantitative separation of microamounts of Mn, Sr and Ba in the presence of other elements with atomic numbers below 84. The method proposed, combined with neutron-activation analysis, has been successfully applied to the simultaneous determination of Mn, Sr and Ba in plant and animal tissues. The method is simple and accurate.

THE existing chemical methods for the separation of Ba, Sr and Mn are based on precipitation, solvent extraction and ion-exchange. A variety of matrices, organic and inorganic, have been analysed for these elements by combined radioactivation and precipitation or precipitation–extraction procedures,[1–3] but these methods are not very convenient for series analyses. The need of a simple and rapid method for the simultaneous determination of Ba, Sr and Mn led to the use of ion-exchange resins combined with radioactivation analysis techniques.

The resin column separation of alkaline earths from one another has been studied by several workers.[4–8] The eluting agents used for this purpose are ammonium salts such as tartrate and lactate.

A fast separation of Ca, Sr and Ba from one another has been achieved by cation-exchange elution with EDTA.[9] On the basis of a general separation Ba and Sr have been isolated from fission products in 6 hr by Tompkins and co-workers.[10] Biological and mineral ore samples have been analysed for Mg, Sr, Ca and Ba by Pollard and co-workers.[11] These authors separated the alkaline earths on cation-exchange resins, using α-hydroxyisobutyric acid as eluting agent, and estimated each alkaline earth by flame spectrophotometry. The ion-exchange separation scheme reported by Aubouin and Laverlochère[12] is suitable for separation following radioactivation of the sample. By the three-column elution technique they separated successively Mn and the long-lived isotopes of Ca, Sr and Ba. The time necessary to perform separations is rather long, so this scheme is not favourable for the analysis of the short-lived isotopes considered here.

This paper describes a simple and rapid ion-exchange radiochemical procedure for the simultaneous separation of Mn, Sr and Ba. The procedure developed, combined with neutron-activation analysis, has been successfully applied to the determination of Mn, Sr and Ba in plant and animal tissues.

EXPERIMENTAL

Reagents

Standard solutions. Solutions of Ba, Sr, Sc and La (1 mg/ml) and Mn (0·1 mg/ml) were prepared by dissolving spectrographically pure Johnson Matthey reagents.

Carrier solution. A solution containing 200 μg each of Ba, Sr, Sc, Mn and La per ml.

Chemicals and solutions. The following analytical grade reagents were also used: hydrochloric acid, 0·1*M*, 1·33*M*, 2*M* and 8*M*; nitric acid, 1·38*M*, 1·75*M* and 6*M*; sulphuric acid, 0·9*M*; hydrogen peroxide, 30% w/v, 100 vol.

Resins. Dowex 1 × 8 and 50W × 8 (100–200 mesh). Fines removed by decantation. Treated with hydrochloric acid and water by the batch equilibration method (6–8 times for every step) as follows: anion-exchange resin: water, 8*M*, 4*M* and 1*M* hydrochloric acid, then water till chloride-free; cation-exchange resin: water, 9*M* and 3*M* hydrochloric acid, then water till chloride-free. The resins were then stored under water.

Apparatus

The ion-exchange columns consisted of borosilicate glass tubes 150 mm long and 6-mm or 12-mm bore, closed at the lower end with a 2-mm bore tube and stop-cock. The resin was supported on a glass-wool bed. Three types of column were prepared and the column volume was calculated on the basis of water-swollen resin.

Column	Resin	Diameter, *mm*	Length, *mm*	Volume, *ml*	Form
1	1 × 8	6	60	1·7	Cl^-
2	50W × 8	6	90	2·5	H^+
3	50W × 8	12	120	13·5	H^+

The columns were finally washed with 10 column-volumes of 8*M* hydrochloric acid for column 1 and of 0·1*M* hydrochloric acid for columns 2 and 3.

All elutions from columns 2 and 3 were performed at a flow-rate of 0·40–0·44 ml/min. A sensitive manometer was used to control the air-pressure applied to these columns during elution. Elutions from column 1 were made at a flow-rate of 2·8–3·2 ml/min.

A pneumatic tube sample transfer system was used to perform irradiations in the reactor of the Nuclear Research Centre "Democritos" at a flux of 2×10^{12}n.cm^{-2}.sec^{-1}. A 400-channel pulse-height analyser in conjunction with a 75 × 75 mm NaI(Tl) crystal was used for counting.

Preliminary experiments

The general ion-exchange studies by Kraus and Nelson,[13] Nelson and co-workers,[14] and Strelow and co-workers[15] provided a basis for this work.

A 90-min test procedure for the separation of Na, Mn, Sr and Ba was developed initially. After fixation of these elements on Dowex 50W × 8 in 0·1*M* hydrochloric acid, sodium was eluted with 4·5 column-volumes (c.v.) of 1·33*M* hydrochloric acid, manganese with 3·5 c.v. of 2*M* hydrochloric acid, strontium with 4·5 c.v. of 2·5*M* hydrochloric acid and finally barium with 3 c.v. of 6*M* nitric acid. Experiments were carried out to discover the optimum conditions.

Elution curves of the elements were studied individually on anion- and cation-exchange resins by elution with 8*M* and 1·33*M* hydrochloric acid solutions respectively. The radioisotopes of the elements tested were ^{24}Na, ^{32}P, ^{38}Cl, ^{42}K, ^{45}Ca, ^{46}Sc, ^{52}V, ^{51}Cr, ^{56}Mn, ^{59}Fe, ^{60}Co, ^{65}Ni, ^{64}Cu, ^{69m}Zn, ^{72}Ga, ^{75}Ge, ^{76}As, ^{75}Se, ^{80}Br, ^{88}Rb, ^{87m}Sr, ^{90}Y, $^{97}\text{Zr} \rightarrow {}^{97}\text{Nb}$, ^{111m}Cd, $^{99}\text{Mo} \rightarrow {}^{99m}\text{Tc}$, ^{101}Tc, ^{116m}In, ^{122}Sb, $^{132}\text{Te} \rightarrow {}^{132}\text{I}$, ^{128}I, ^{134m}Cs, ^{139}Ba, ^{140}La, ^{153}Sm, ^{151}Eu, ^{166}Ho, ^{177}Lu, ^{180m}Hf, ^{182}Ta, ^{187}W, ^{188}Re, ^{198}Au and $^{197+197m}$Hg.

The results obtained and the conclusions drawn from the experiments on elution behaviour led to the final separation of Mn, Sr, Ba, Sc and the rare earth group from one another. Several mineral acids were tested as eluents.

Procedure

Preparation and irradiation of samples and standards. Animal tissues are dried at 150° for 20 hr and ashed at 550° until a white powder is obtained. Plant tissues are dried at 95° for 20 hr and at 200° for 3 hr. Finally the tissues are ashed at 550° until a white powder is obtained.

The sample (30–100 mg of ash) and 0·5 ml of a mixture of standard solutions are transferred into 1-ml polyethylene vials and sealed. The mixture of standards contains 0·1 ml each of Mn, Sr, Ba, Sc and La solutions. Sample and standards are irradiated together in the pile at a flux of 2×10^{12} n.cm^{-2}.sec^{-1} for 30 min. (Plant tissues were irradiated for 2 hr at the same flux.) The (n, γ) reactions produced on stable isotopes by thermal neutrons are used. The properties[16] associated with the reactions considered are summarized in Table I. Interference by fast neutron reactions is insignificant as long as the target elements do not constitute the matrix of the sample.

Analytical procedure. After irradiation the sample is opened and transferred to a 100-ml beaker. One or two drops of the carrier solution, 2 ml of 8*M* hydrochloric acid and 0·3 ml of hydrogen peroxide are added. The resulting solution is evaporated almost to dryness on a hot-plate. Then 2 ml of 8*M* hydrochloric acid are added and the beaker is heated until the solution is clear. The solution is transferred to the top of column 1, the beaker being rinsed twice with about 0·5 ml of 8*M* hydrochloric acid. Elution is carried out with 9 ml of 8*M* hydrochloric acid. The total effluent is collected in a 100-ml beaker and evaporated to 0·5 ml on a hot-plate. Then 1·5 ml of water and 0·5 ml of hydrogen peroxide are added and the solution evaporated to 0·5 ml, 2 ml of water are added and evaporated off again (this step is repeated twice more), and finally 2 ml of water are added.

TABLE I.—NUCLEAR DATA OF THE ELEMENTS ESTIMATED

Stable isotope	Abundance %	Cross-section, *barn*	Isotope produced	Half-life, *hr*	γ-Ray, *keV*	Possible interfering reactions
^{138}Ba	71·66	0·5	^{139}Ba	1·4	165	^{139}La(n, p)^{139}Ba ^{142}Ce(n, α)^{139}Ba
^{86}Sr	9·86	1·3	^{87m}Sr	2·8	390	^{90}Zr(n, α)^{87m}Sr
^{55}Mn	100·00	13·3	^{56}Mn	2·57	840	^{56}Fe(n, p)^{56}Mn ^{59}Co(n, α)^{56}Mn
^{139}La	99·90	8·2	^{140}La	40·2	1600	^{140}Ce(n, p)^{140}La ^{138}Ba(n, γ)^{139}Ba$\xrightarrow{\beta}$ $\rightarrow$^{139}La(n, γ)^{140}La
^{45}Sc	100·00	10·4 + 12·0	^{46m}Sc + ^{46}Sc	2·013	885	^{46}Ti(n, p)^{46}Sc

The resulting solution is transferred to column 2 (column 3 for plant tissues). The beaker is washed three times with 0·5 ml (1 ml)* of 0·1*M* hydrochloric acid and the washings are transferred to the column. Sodium is eluted with 11·5 ml (50 ml) of 1·33*M* hydrochloric acid and the effluent is discarded. Manganese is then eluted with 9 ml (35 ml) of 2*M* hydrochloric acid and collected for counting. Strontium and barium are successively eluted with 19 ml (100 ml) of 1·38*M* nitric acid and 14 ml (55 ml) of 1·75*M* nitric acid and collected for counting. Scandium and the rare earths are eluted quantitatively with 18 ml of 0·9*M* sulphuric acid and 12 ml of 6*M* nitric acid respectively. From the irradiated standard solution mixture, 0·25 ml is transferred to a 100-ml beaker containing 2 ml of 8*M* hydrochloric acid and 0·3 ml of hydrogen peroxide. The solution is heated to remove the hydrogen peroxide and transferred to column 1. It is then processed in the same manner as the sample. Sample and standards are analysed at the same time.

Radioactivity measurements. The column effluent fractions containing the separated radioisotopes are counted directly by means of a multichannel analyser. The γ-ray measurements are evaluated by the method of Covell.[17] The results obtained by elution of Mn, Sr, Ba, Sc and rare earths indicate a recovery better than 99·8%. A γ-ray examination and a half-life determination are made on the isolated short-lived radioisotopes to check their radiochemical purity whenever unknown samples are analysed.

RESULTS AND DISCUSSION

The main purpose of the method is the radiochemical isolation of ^{139}Ba, ^{87m}Sr and ^{56}Mn from a mixture containing other elements, in a reasonable period of time. It would appear that the 100–200 mesh resin Dowex 50W × 8 presents the optimum combination of quick elution and good separation factors.

The elements Mn, Sr and Ba are not retained on the anion-exchange resin in hydrochloric acid, but a number of others are. The effect is reversed on cation-exchange resins where many elements are eluted with dilute hydrochloric acid while Mn, Sr and Ba show rather high distribution coefficients. On the basis of a purely chemical separation, the elution behaviour of elements having atomic numbers below 84 was studied, first on a Dowex 1 × 8 column in 8*M* hydrochloric acid and then on a Dowex 50W × 8 column in 1·33*M* hydrochloric acid. The results were in good agreement with those reported previously.[13,14] The elution behaviour of the elements

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* Quantities in brackets refer to plant tissue analysis.

not tested on the columns was estimated by the values of their distribution coefficients[13,14] in comparison with those of the elements tested.

On the anion-exchange resin the following elements are retained completely—Fe, Co, Cu, Zn, Ga, Ge, Cd, Mo, Tc, Sb, Te, W, Re, Au, Hg—and these partially—In (50%), Ta (80%), Se (5%), Zr (34%), Hf (34%). The elements not retained on either anion- or cation-exchange columns were P, Cl, V, As, Br, I. Cr (18%), Se (95%), Ta (20%), In (20%), Zr (10%) and Hf (10%) are partially retained on the cation-exchanger.

It was found that the elements still retained on the cation resin after elution with 1·33*M* hydrochloric acid are Mn, Sr, Ba, Sc, rare earths, Y, Ni, Rb, Mg, Al, Ca, Be, Cs, K and partially Cr, Ti, Hf and Zr.

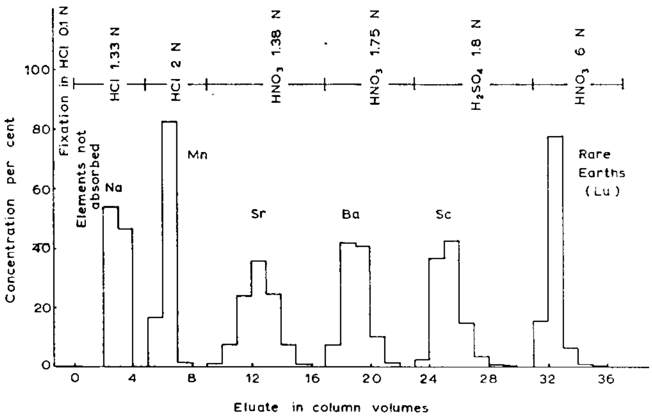

FIG. 1.—Sequential elution scheme.

The γ-activity of the radioisotopes of Y, Ni, Rb, Mg, Al, Ca, Be, Ti and Zr formed by thermal neutrons falls to background levels in 3 hr from the end of the irradiation, for the following reasons: short half-lives of ^{27}Mg, ^{28}Al, ^{49}Ca, ^{51}Ti and ^{88}Rb; negligible γ-activity of ^{65}Ni and ^{90m}Y, and no γ-activity of ^{90}Y and ^{45}Ca; no significant formation of ^{95}Zr–^{95}Nb, ^{97}Zr–^{97}Nb, ^{86}Rb and ^{10}Be, owing to the low activation cross-section of their corresponding stable isotopes or to the short irradiation time used.

It should be noted that Y is eluted after the Ba separation. Thus ^{90m}Y could only interfere with the rare earths. On the other hand the bremsstrahlung resulting from the ^{90}Y β-particles could interfere with rare earths having γ-energies less than 250 keV.

The remaining elements are sequentially separated by the chromatographic elution scheme (as given in Fig. 1).

In this scheme the separation of K and Cs was not undertaken because the necessary preliminary elution steps influence the Ba sensitivity. However, 75% of the caesium is eluted with the manganese and 25% with the strontium, but the radioisotope formed, ^{134m}Cs, has a low γ-energy (128 keV) and does not interfere with ^{56}Mn and ^{87m}Sr counting. Also ^{42}K is 30% eluted with Na and 70% with Mn, and does not affect ^{56}Mn counting when its Compton counting rate is deducted from the Mn peak by the method of Covell. Finally ^{51}Cr and ^{180m}Hf are eluted continuously during all elution procedures. The Compton effect and γ-ray interference of ^{51}Cr on ^{139}Ba and ^{87m}Sr may be eliminated by another counting and subtraction after one day.

Then the precision and sensitivity of the ^{139}Ba and ^{87m}Sr measurements may be affected according to the ^{51}Cr concentration in the sample. Thus, ^{180m}Hf remains as the main interfering nuclide.

It should be noted that lutetium is used in the presentation of elution conditions (Fig. 1) but the determination of lanthanum is discussed in the text. This is done because lutetium shows a lower distribution coefficient value in the media used. Consequently it is clear that no rare earth has an elution curve that overlaps with that of scandium. Nitric acid was a good eluent for the separation of strontium and barium (Fig. 1) but not for the elution of scandium. The separation of scandium with 14 column volumes of 2*N* nitric acid does not give a sharp elution curve; for this reason nitric acid was replaced with sulphuric acid in this step.

TABLE II.—TEST OF THE ION-EXCHANGE SEPARATION METHOD

Sample	Mn, *μg*		Sr, *μg*		Ba, *μg*		Sc, *μg*	
	Added	Found	Added	Found	Added	Found	Added	Found
1	10	10·29	100	95·7	100	105·9	100	98·2
2		9·51		98·2		94·0		98·5
3		9·90		102·2		99·6		97·1
4		10·29		104·2		98·6		103·0
5		10·00		100·0		100·0		100·0
6		9·66		99·1		97·4		102·0
7		10·08		96·8		102·9		98·8
8		10·24		100·9		102·4		99·6
Mean		9·99		99·6		100·1		99·6
Standard error		±3·5%		±2·8%		±3·7%		±2·0%

An attempt was made to precipitate barium and strontium on the resin after the elution of manganese and to elute the other cations with sulphuric acid (2 or 3*M*). Strontium could then be eluted with 2·5*M* hydrochloric acid and barium with 6*M* nitric acid. It was noted that strontium appeared in the effluent, probably by dissolution, before lanthanum was completely eluted. The elution curves given in Fig. 1 are applicable up to 200 *μ*g weight of each element separated, and any other individual element of the sample to be analysed should not exceed this amount.

It is known that on the anion resin in 8*M* hydrochloric acid, copper has a low distribution coefficient value and antimony shows a tendency to hydrolyse. However, the separation factor for these elements from Mn, Sr, Ba, Sc and rare earths was about 10^4.

The method was tested by analysing samples of known composition. Eight sample solutions were prepared by mixing known quantities of ^{56}Mn ^{87m}Sr, ^{139}Ba and ^{46}Sc. The samples were analysed, sample 5 being a weight and activity reference standard. Table II shows that the method gives good reproducibility.

Animal tissues analysis

Application of the method to animal tissues was made by determining Mn, Sr and Ba in a tunicate species of marine organism available in the laboratory (Table III). The results for Ba show a higher standard deviation than do those in Table II, and

TABLE III.—ANIMAL TISSUE ANALYSIS (TUNICATE SPECIES)

Sample	Amount of element in 100 mg of ash, μg		
	Mn	Sr	Ba
1	193·7	31·6	2·1
2	185·5	29·2	1·9
3	189·4	29·3	2·3
4	196·6	32·6	2·6
5	190·0	30·7	2·2
6	177·1	29·8	2·5
7	183·5	34·7	1·9
8	195·2	33·2	2·2
Mean	188·8	31·4	2·2
Standard error	±3·5%	±6·4%	±12%

this is not due to the irradiation error, but to the fact that the quantities of barium determined are in the region of the sensitivity limits.

Effect of major constituents

Any other element except Mn, Sr, Ba, Sc and the rare earths is considered as an impurity. A sample impurity in amounts of more than 200 μg constitutes a major constituent and its presence may cause serious errors on account of (*a*) incomplete separation and consequent contamination of an isolated radioisotope, (*b*) saturation of the column and column exclusion of one or more elements to be eluted.

In this case the two effects may be obviated by simply increasing the dimensions of the appropriate column, depending on the major constituent, and scaling up the resin volume accordingly. Hydrolysis of large amounts of niobium and tantalum can be prevented by making the 6*M* hydrochloric acid 0·01*M* in hydrofluoric acid.

It would appear that any other element having an atomic number below 84, except those reported, should have no influence on the analytical procedure. Matrices are considered as major constituents and impose the same limitations. Consequently the analysis of a Li, V, Mo, Re, Ir, P, As, Se or Te matrix is possible by direct application of the method. Application to other matrices is possible if the volume of the appropriate column is increased.

Comparison of results on standard samples

The accuracy of the method was tested by analysing the ash of six standard kale powder samples. The results obtained were compared with those given by Bowen[18] (Table IV).

The ion-exchange method described appears to be quite satisfactory for the elements determined. It is known that considerable amounts of Ca and K are present in plant tissues. Bowen[18] reports for kale, 41400 ppm of Ca, 24600 ppm of K and 1600 ppm of Mg. Since the sample weight used was about 0·3 g, so that major components were important, the normal column size was modified. The time for a complete analysis, after irradiation, was then increased to 4 hr.

TABLE IV.—PLANT TISSUES ANALYSIS (KALE)

Sample	Mn, *ppm*		Sr, *ppm*		Ba, *ppm*	
	Found	Reference value	Found	Reference value	Found	Reference value
1	14·5	14·9 ± 1·8	86·4	84·1 ± 10·7	4·7	4·58 ± 0·54
2	14·7		92·0		5·0	
3	15·2		79·0		3·9	
4	16·8		88·5		4·4	
5	14·0		82·1		4·9	
6	16·5		91·0		4·0	
Mean value	15·3		86·5		4·5	
Standard error	±7·1%		±5·9%		±10·2%	

Analysis in series

The determination of Ba, Sr and Mn is possible in twelve samples simultaneously by one operator. After irradiation, the time necessary to perform a complete analysis with columns of normal size is about 4 hr. It was found that the standard error due to the irradiation is ±5% when six samples in vials of 1-ml capacity are irradiated together with one standard in a central position. Thus the standard error of an analysis should be lower than ±10% for the elements under consideration, provided that the detection limits are not reached.

Sensitivities

The limit of detection of the elements irradiated for 30 min in a 2×10^{12} n.cm^{-2}.sec^{-1} thermal neutron flux was found by γ-counting of the radioisotopes ^{56}Mn, ^{87m}Sr, ^{139}Ba, ^{46}Sc and ^{140}La 4 hr after the end of irradiation. The detection limit is defined as the amount of the element providing a count-rate twice the background level. Thus a limit of 2 μg was found for Ba and Sr, 0·01 μg for Mn and 1 μg for Sc and La. Some of the other rare earths are even more sensitive than La, but it is not always easy to determine them in a rare earth mixture. However, lanthanum is easier to determine because of a higher γ-energy value.

The method is convenient for sample series analysis and faster than the similar ion-exchange separation methods for determining Sr, Ba or Sr, Ba, Mn in a mixture. The recovery of these elements was better than 99·8%. For this reason carriers were not used for determining the chemical yield of the separated elements. Carrier-free separation of traces of these elements is possible in principle. However, 10–20 μg of carrier for each element determined were used, because the minimum amount tested in each case was 10 μg.

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Zusammenfassung—Eine schnelle radiochemische Ionenaustauschmethode zur quantitativen Trennung von Mikromengen Mn, Sr und Ba in Gegenwart anderer Elemente mit Ordnungszahlen unter 84 wurde entwickelt. Die vorgeschlagene Methode wurde in Kombination mit Neutronenaktivierungsanalyse erfolgreich zur gleichzeitigen Bestimmung von Mn, Sr und Ba in pflanzlichem und tierischem Gewebe verwendet. Die Methode ist einfach und genau.

Résumé—On a élaboré une méthode d'échange d'ions radiochimique rapide pour la séparation quantitative de microquantitiés de Mn, Sr et Ba en présence d'autres éléments de nombres atomiques inférieurs à 84. La méthode proposée, combinée à l'analyse par activation de neutrons, a été appliquée avec succès à détermination simultanée de Mn, Sr et Ba dans les tissus végétaux et animaux. La méthode est simple et précise.

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ANALYSIS OF ISOTOPIC RADIUM IN THORIUM MILL EFFLUENTS

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Summary—A simple and rapid method has been developed for the determination of isotopic radium, based on γ-ray spectrometry. ^{228}Ra and ^{224}Ra are assayed by measuring the intensities of the photo-peaks in the 0·94 and the 2·62 MeV regions of the γ-spectrum. The interference in these measurements, arising from the presence of the ^{226}Ra–^{210}Pb chain in the sample, is obviated by the almost complete expulsion of ^{222}Rn from the system. The precision of the method is $\pm 2\%$ and $\pm 3\%$ in the determination of ^{228}Ra and ^{224}Ra respectively, the absolute sensitivities being 2 and 0·5 nCi. The method has been applied to evaluate the distribution of these isotopes in the various products of the Indian Rare-Earths Factory, Alwaye.

A KNOWLEDGE of the distribution of radium-228 and -226 at various stages of chemical operations in thorium and uranium plants is necessary from the point of view of evaluating recoveries and health hazards.[1,2] The concentration of radium-224 in aged effluents of a thorium plant enables evaluation of the content of thorium-228 which can serve as a "cow" for radium, lead and bismuth activities, to be used in tracer studies. This isotope also finds use as an α-tracer[3] and is of interest for use in a proposed portable neutron source.[4,5] Determination of radium-228 and -224 in pure thorium compounds gives an estimate of the status of radioactive equilibrium of the thorium-232 series in these compounds.

Methods used and recommended for the determination of radium isotopes, present either alone or as a mixture of isotopes, have been reviewed by Sedlet.[6] These methods, however, are not simple or non-destructive and so are not suitable for the continuous analysis as is required in a plant. This paper presents such a method for radium-228 and -224, and was applied to the determination of these isotopes in various products of the Indian Rare-Earths Factory at Alwaye.

The γ-ray spectra of the three radium isotopes, 224, 226 and 228, in equilibrium with their daughter products, are shown in Fig. 1. In principle, the individual radium isotopes can be determined by measuring the intensities of photo-peaks in the characteristic regions of the γ-spectra, and then setting up a series of simultaneous equations. The constants for solving these equations can be determined from pure systems, provided the relative retention of the emanations (^{222}Rn and ^{220}Rn) is the same in the sample and the standard. But in practical systems, this may not be valid. The retention of radon is dependent on the temperature, and on the nature of the solvent and the concentration of the solution.[7] These factors are not of any consequence in the case of radon-220, because of its short half-life ($t_{1/2} = 54$ sec). However, the precision of such determinations becomes poorer the larger the number of unknowns involved.[8,9]

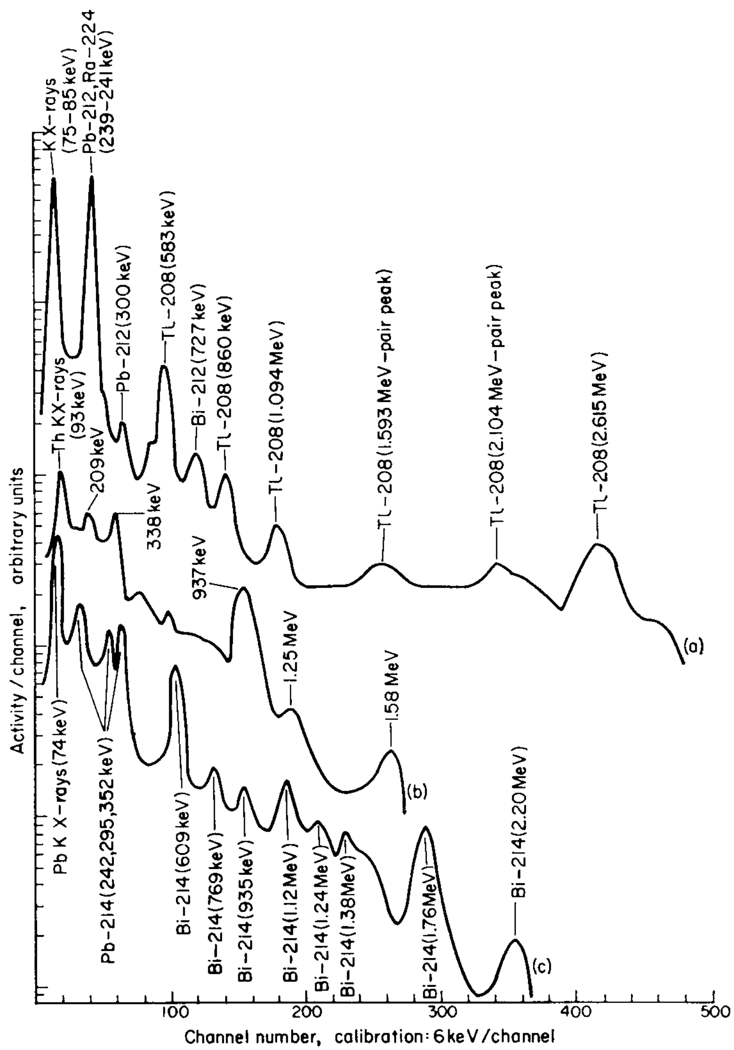

FIG. 1.—Gamma-ray spectra: (*a*) ^{224}Ra and decay products; (*b*) ^{228}Ra–^{228}Ac; (*c*) ^{226}Ra and decay products.

To obviate these difficulties, the daughter products of radium-226, which are mainly responsible for the γ-activity exhibited by the radium-226–lead-210 chain, were eliminated by the almost complete expulsion of radon-222 from the system under study.

Under these conditions, the measured γ-activities under the photo-peaks of interest can be related by the equations

$$R_1 = K_1 C_{(2 \cdot 6)} \tag{1}$$

$$R_2 = K_2[C_{(0 \cdot 94)} - C_{(2 \cdot 6)}\theta] \tag{2}$$

where R_1 and R_2 are the respective amounts of radium-224 and -228 (in nCi), K_1 and K_2 are the experimental constants, *viz.*, nCi of radium-224 and -228 giving 10^4 cpm under the respective photo-peaks, $C_{(2\cdot6)}$ and $C_{(0\cdot94)}$ are the observed count-rates (cpm) under the 2·6-MeV and 0·94-MeV peaks respectively, and θ is the ratio of the activity of the radium-224–lead-208 chain in the 0·94-MeV region to that in the 2·6-MeV region.

EXPERIMENTAL

Expulsion of radon-222 from the sample solution

Aliquots of radium-226 solution in dilute nitric acid were boiled for a period ranging from 1 to 4 hr, immediately cooled in an ice-bath, made up to 50 ml and transferred to one of the matched stoppered conical flasks (see *Procedure*). The integrated γ-activity with energy above 0·34 MeV was followed.

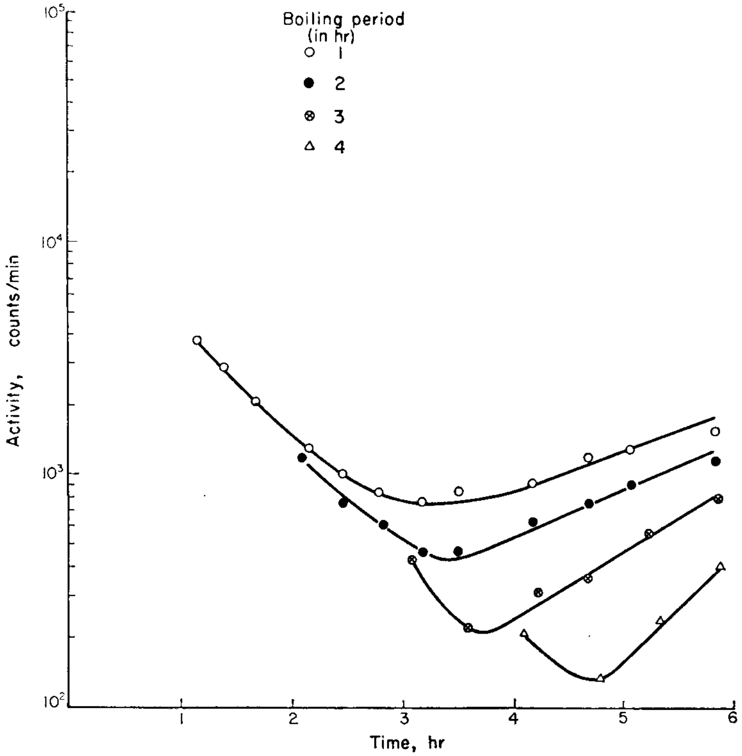

FIG. 2.—Expulsion of ^{222}Ra as a function of boiling-period.

Figure 2 shows that the minimum activity progressively decreases with increase in boiling time. From the minimum activity relative to the initial activity of an equal aliquot stored for a month in another matched flask, the apparent retention of radon-222 was calculated and is given in column 3 of Table I. The last column of this table gives the retention calculated on the basis of the activity measured 1 hr after the time of minimum activity, in order to assess the extent of growth of the daughter products of radium-226 at the end of an hour, which is approximately the time taken for the analysis.

It can be deduced that more than 96% of the radon can be removed by boiling the solution for about 3 hr. Further boiling does not expel radon to any appreciable extent.

Procedure

The γ-activity measurements were made on the samples in solution, contained in 150-ml stoppered conical flasks. These flasks were matched by transferring into them 50-ml aliquots of an aged rare-earth chloride effluent from the Indian Rare Earths plant and measuring the gross γ-activity of the aliquots. Only those flasks which gave γ-activity values within two standard deviations of the mean were accepted for use.

TABLE I.—EXPULSION OF ^{222}Rn FROM THE SYSTEM

Boiling period, hr	Retention, % Corresponding to minimum observed activity (time t) of	Retention, % Corresponding to $t + 1$ hr
1	4·5	5·5
2	2·4	3·6
3	1·8	3·3
4	1·0	2·4

Solid samples were dissolved by suitable means (*e.g.*, acid attack or fusion with a suitable flux followed by dissolution in acid). Then 50 ml of sample solution were boiled in a 250-ml beaker for 3 hr. Water was added from time to time to keep the volume of the solution ~50 ml. The solution was cooled to room temperature by means of an ice-bath, then made up to 50 ml and drained into one of the matched flasks. The γ-activity under the 2·62-MeV and 0·94-MeV peaks was measured, starting 30 min after the boiling was stopped. The experimental constants K_1, K_2 and θ were evaluated each time before and after the samples were counted, to check the stability of the counting apparatus.

RESULTS

Evaluation of K_1, K_2 *and* θ

The experimental constants K_1 and K_2 were evaluated with solutions of a monazite and a uranothorianite mineral containing respectively 7·6 and 67·0% of thorium. The constant θ was evaluated by means of lead-212 in equilibrium with its daughters. The lead-212 activity was obtained by isolating it from thorium nitrate according to the method reported by Parekh and Sankar Das.[10] The values obtained for K_1 and K_2 are presented in Table II; θ was found to be 1·40 ± 0·05.

TABLE II.—EXPERIMENTAL CONSTANTS K_1 AND K_2

Sample	K_1	K_2	^{228}Ra	^{224}Ra
	nCi/10^4 *cpm*		*nCi*/*g* Th*	*nCi*/*g* Th*
Monazite	835	160	—	—
	800	162	—	—
Urano-thorianite	796	151	116	112
	822	155	113	108
	776	155	113	115
	798	155	113	112
	774	160	110	115
			Mean 113 ± 2	112 ± 3

* Calculated ^{228}Ra and ^{224}Ra per g of thorium = 109 nCi.

Various products obtained from two batches of monazites processed at the Indian Rare Earths Factory, Alwaye[11] were analysed for their radium-228 and -224 contents. Table III records the results.

These isotopes were also assayed in the other products of this factory, *e.g.*, phosphate solution, mother liquor and trisodium phosphate crystals, and were found to be absent.

The calibration constants K_1, K_2 and θ should ideally be determined from pure decay chains of these isotopes. In the present studies θ was evaluated with the pure system, but in the absence of either standard sources of radium-228 and -224 or

TABLE III.—ANALYSIS OF ^{228}Ra AND ^{224}Ra IN IRE PRODUCTS

	Batch No. 3472*				Batch No. 3473*			
	^{228}Ra	^{224}Ra	Distribution %		^{228}Ra	^{224}Ra	Distribution %	
Sample	*nCi/g*	*nCi/g*	^{228}Ra	^{224}Ra	*nCi/g*	*nCi/g*	^{228}Ra	^{224}Ra
Rare-earth chlorides (normal)	6·08	p. nil	73·4	—	6·43	p. nil	77·6	—
Rare-earth chlorides (lead-free)	6·08	p. nil	73·4	—	6·78	p. nil	81·9	—
Thorium cake	p. nil	8·46	—	101·3	p. nil	8·36	—	100·1
Lead sulphide	0·029	0·083	0·35	1·01	0·024	0·19	0·29	2·25

* ThO_2 8·7%; RE_2O_3 59·4%; P_2O_5 27·0%; PbO 0·26%.
p. nil = practically nil.

uranium-free thorium minerals, monazite with a thorium:uranium ratio of 24 was selected for evaluation of K_1 and K_2. From these constants, the radium-228 and -224 contents of the uranothorianite mineral (thorium : uranium ratio 4) has been calculated and is given in the last two columns of Table II. It is seen from these results that the precision of the method is ±2% and ±3% in the determination of radium-228 and -224 respectively. The mean values of 113 and 112 nCi per g of thorium compare well with the theoretical value of 109 nCi/g. The positive bias, though small, is attributed to the higher amount of radon-222 residual in the solution of this sample, compared to that of the monazite.

Table III shows that about 77% of the radium-228 is concentrated in the rare-earth chlorides solution (both normal and lead-free). Thorium concentrate, lead sulphide and phosphates do not contain this isotope to any appreciable extent. As should be expected, radium-224 was not detectable in the rare-earth chlorides, since this isotope, in the absence of its immediate parent thorium-228 in these solutions, decayed completely during the month that elapsed between the processing and the analysis of these samples ($t_{1/2}$ ^{224}Ra = 3·64 d). However, this isotope was found to be in equilibrium abundance in the thorium concentrates, the equilibrium activity being 8·35 nCi/g of the monazite.

The absolute sensitivity of the method expressed as that concentration of the isotope which gives an observed activity equal to the background activity under a fixed set of experimental conditions is 2·0 and 0·5 nCi for radium-228 and -224 respectively. The major advantages of this method are its simplicity, rapidity and easy adaptability in a plant process.

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Zusammenfassung—Ein einfaches und schnelles Verfahren zur gammaspektrometrischen Bestimmung von isotopem Radium wurde entwickelt. ^{228}Ra und ^{224}Ra werden durch Messung der Intensität der Photopeaks im Gebiet um 0,94 bzw. 2,62 MeV des Gammaspektrums bestimmt. Die Störung dieser Messungen durch die Anwesenheit der Kette ^{226}Ra–^{210}Pb in der Probe wird umgangen durch das fast vollständige Austreiben von ^{222}Rn aus der Probe. Die Genauigkeit der Methode beträgt ±2% und ±3% für ^{228}Ra bzw. ^{224}Ra; die Absolutempfindlichkeiten sind 2 und 0,5 nCi. Die Methode wurde zur Ermittlung der Verteilung dieser Isotope in den Produkten der Indian Rare-Earths Factory in Alwaye angewandt.

Résumé—On a élaboré une méthode simple et rapide pour la détermination du radium isotopique, basée sur la spectrométrie γ. ^{228}Ra et ^{224}Ra sont titrés par mesure des intensités des photo-maximums dans les régions 0,94 et 2,62 MeV du spectre γ. L'interférence dans ces mesures, provenant de la présence de la chaîne ^{226}Ra–^{210}Pb dans l'échantillon, est évitée par l'expulsion presque totale de ^{222}Rn du système. La précision de la méthode est $\pm 2\%$ et $\pm 3\%$ dans le dosage de ^{228}Ra et ^{224}Ra respectivent, les sensibilités absolues étant 2 et 0,5 nCi. On a appliqué la méthode pour évaluer la distribution de ces isotopes dans les divers produits de l'Indian Rare-Earths Factory, Alwaye.

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ANWENDUNG DER RÖNTGENFLUORESZENZ IN DER SPURENANALYSE—II*

ANREICHERUNG VON SPURENMETALLEN DURCH FÄLLUNG MIT 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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Zusammenfassung—Bis zu maximal 100 μg der Metalle Mangan, Eisen, Kobalt, Nickel, Kupfer und Zink werden durch Zugabe einer alkoholischen PAN-Lösung bei pH 10 gefällt. Der Niederschlag wird auf einem Filterpapierscheibchen gesammelt, getrocknet und samt dem Filterpapier direkt in die Röntgenfluoreszenzapparatur gebracht. Zwischen Metallmengen bis zu 100 μg und den registrierten Impulsen an den jeweiligen Kα-Linien besteht strenge Proportionalität. Eine gegenseitige Beeinflussung konnte nicht festgestellt werden. Für die oben genannten Metalle werden Meßempfindlichkeit, Richtigkeit und Reproduzierbarkeit der Messungen, sowie die Erfassungsgrenzen angegeben. Die letzteren betragen je nach Metall 0,1 bis 0,5 μg in einem Volumen von rund 50 ml. Praktische Anwendungsmöglichkeiten des Verfahrens werden diskutiert.

AUF die grundsätzliche Bedeutung und Leistungsfähigkeit der Röntgenfluoreszenzanalyse für die quantitative Bestimmung geringster Mengen und Konzentrationen von Elementen wurde bereits im ersten Teil hingewiesen;[1] im besonderen wurde dort die extraktive Anreicherung von Metallspuren behandelt.

Einem Vorschlag von Liebhafsky *et al.*[2] entsprechend teilt man Proben, in welchen Spurenelemente mittels Röntgenfluoreszenz bestimmt werden sollen, zweckmäßig in zwei Kategorien ein: Kategorie I umfaßt Proben, welche die zu bestimmenden Elemente in geringsten Konzentrationen enthalten, wobei eine größere Probenmenge zur Verfügung steht, und Kategorie II solche, welche die zu bestimmenden Elemente zwar in höherer Konzentration enthalten, wobei aber nur eine geringe Probenmenge verfügbar ist.

Bei Proben der ersten Kategorie hängt die geringste in einer Probe noch meßbare Konzentration eines Elements (d.i. die Grenzkonzentration[3]) sehr wesentlich vom Probenmaterial ab. Die Ordnungszahl des Matrixmaterials beeinflußt stark die Grenzkonzentration und die Empfindlichkeit der Messung. Dieser Umstand setzt dem Verlangen, Spurenelemente in einer beliebigen Probe *direkt* zu bestimmen, eine natürliche Grenze. Man muß daher häufig—speziell bei Vorliegen von Proben mit schwerer Matrix—die Spuren von der Matrix trennen, anreichern, und so in Proben der zweiten Kategorie überführen, wo sie auf einfache Weise bestimmt werden können.

Als Mittel zur Anreicherung von Spuren für eine nachfolgende Röntgenfluoreszenzanalyse wurden in der Literatur bisher Ionenaustauschermembranen,[4,5] Ionenaustauscherpapiere,[6–10] feste Ionenaustauscher,[11,12] mit spezifischen Reagenzien

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* Mitteilung I—*Mikrochim. Acta*, 1965, 770.

imprägniertes Filterpapier[13] und kürzlich auch die Extraktion[1] beschrieben. Dieses Verfahren bietet zahlreiche Vorteile, insbesondere die hohe Reproduzierbarkeit der Ergebnisse, und die niedere Erfassungsgrenze.

Ein gewisser Nachteil ergibt sich aber aus der Notwendigkeit, den gewonnenen Extrakt auf einer kleinen Fläche einzudampfen. Unter Verwendung eines Ringofens und von Filterpapier als Probenträger, können maximal 2 ml/Stunde eingedampft werden. Eine wesentliche Erhöhung der Eindampfgeschwindigkeit bietet die Verwendung eines Trägers aus Reinstaluminium.[1] Doch auch hier wird es schwierig, sobald eine größere Rückstandsmenge anfällt; der Rückstand beginnt auf dem Probenträger zu klettern, was eine schlechte Reproduzierbarkeit der geometrischen Verhältnisse verursacht.

Eine vielversprechende Möglichkeit, Mikrogramm-Mengen von Metallen anzureichern, bietet die Fällung mit organischen Reagenzien. Fagel, Balis und Bronk[14] haben bei der Analyse von festem Alkalicarbonat 10^{-2} bis $10^{-3}\%$ verschiedener Schwermetalle durch Fällung mittels 8-Oxychinolin angereichert und nachfolgend mit Hilfe der Röntgenfluoreszenzanalyse bestimmt. Hierbei war es notwendig, größere Mengen an Niederschlag zu gewinnen, um daraus Tabletten pressen zu können.[14] Lytle, Dye und Seim[15] haben Metallspuren in pflanzlichem Material durch eine Kombination verschiedener organischer Reagenzien gefällt unter Zugabe von 50 mg Aluminium als Spurenfänger. Die erhaltenen Niederschläge wurden verascht, die Metallspuren in der Asche wurden röntgenspektrometrisch bestimmt. Hirokawa und Goto[16,17] haben Eisen- und Kobalt-, sowie Thorium- und Uranspuren mit Alizarinblau angereichert. Kriege und Rudolph[18] berichten über die Fällung von Zirkoniumspuren mit Brommandelsäure. Diese Autoren sammeln den Niederschlag auf einem Kunststoffilter und bringen ihn anschließend *direkt* im Röntgenfluoreszenz-Gerät zur Messung.

Zweck unserer Untersuchungen war es, die *direkte* Technik näher zu studieren. In der vorliegenden Arbeit werden folgende Fragen behandelt: Wahl des Fällungsmittels, absolute bestimmbare Mengen, gegenseitige Beeinflussung mehrerer Elemente, Linearität der Eichkurven, sowie Richtigkeit und Reproduzierbarkeit.

Wahl des Fällungsmittels

Fällungsmittel zur Anreicherung von Metallspuren sollten folgende Eigenschaften haben: Da die Röntgenfluoreszenz-Spurenanalyse die gleichzeitige Bestimmung mehrerer Metalle nebeneinander gestattet, sofern ihre Mengen voneinander nicht allzu sehr verschieden sind (gegenseitige Beeinflussung), werden zweckmäßigerweise *Gruppenfällungsmittel* anzuwenden sein. Bei diesen sollte es möglich sein, durch einfache Variation der Fällungsbedingungen (pH, Maskierungsmittel) gegebenenfalls die Selektivität zu erhöhen. Selbstverständlich ist bei der Auswahl des Reagenzes darauf zu achten, daß es mit den Matrixelementen keine schwerlöslichen Niederschläge bilden darf. Aber auch die Bildung löslicher Komplexe, die nicht in den Niederschlag gelangen, können wegen eines unkontrollierbaren Reagenzverbrauchs zu Komplikationen führen. Das quantitative Ausfallen der gewünschten Spurenmetalle mit dem gewählten Reagenz muß für die jeweils herrschenden Analysenbedingungen gesichert sein; es wird daher noch in vielen Fällen zu prüfen sein, ob nicht Bestandteile der Analysenlösungen, vor allem komplexbildende Verbindungen (Acetat, Tartrat usw.), Störungen verursachen. Auch Störungen durch Komplexbildung mit

Anionen der Matrixelemente (Wolfram, Molybdän u. dgl.) können gelegentlich auftreten.

In der Regel wird man unter Zusatz eines geeigneten Metalls als Spurenfänger arbeiten müssen, wobei die zugesetzte Menge nicht höher als unbedingt nötig gewählt werden soll. Der Spurenfänger findet sich nämlich quantitativ im Niederschlag und seine Konzentration darin ist um vieles höher als die der gesuchten Metallspuren. Dies verringert die Fluoreszenzstrahlung—die Erfassungsgrenze steigt mit dem Gehalt an Spurenfängermetall an. Wünschenswert wäre es, ohne Zusatz an Kollektormetall arbeiten zu können, d.h. das Reagens selbst müßte die Eigenschaften von Fällungsmittel und Spurenfänger in sich vereinen.

Kürzlich konnten wir berichten, daß das 1-(2-Pyridylazo)-2-naphthol (PAN) diese seltene Kombination von Eigenschaften aufweist und zur Fällung von Mikrogramm-mengen verschiedener Metallionen ohne Kollektorzusatz geeignet ist.[20] Die vorliegende Arbeit befaßt sich daher mit der Möglichkeit, mit Hilfe von PAN Mikrogrammengen verschiedener Metalle ohne Zusatz eines Spurenfängers auszufällen und den erhaltenen Niederschlag *direkt*, d.h. ohne weitere Manipulation, der Röntgenspektralanalyse zuzuführen.

Das Verfahren

Das von uns vorgeschlagene Verfahren besteht darin, die Metallspuren aus einer wässrigen Lösung durch Zugabe von PAN zu fällen, den erhaltenen Niederschlag auf einem Blättchen Filterpapier zu sammeln, zu trocknen und anschließend den auf dem Papier haftenden Niederschlag direkt mit Hilfe der Röntgenfluoreszenzanalyse zu untersuchen. Nähere Einzelheiten über Fällungs- und Meßbedingungen sind im experimentellen Teil zusammengefaßt.

Die Fällung von mehrwertigen Metallionen durch PAN ist schon länger bekannt,[21] jedoch erst kürzlich näher untersucht und für analytische Zwecke angewendet worden. Bezüglich der Fällbarkeit ausgewählter Metallionen und der Wirkung von PAN als Fällungsmittel und Spurenfänger zugleich sei auf diese Arbeit im Original hingewiesen.[20] Es soll hier wiederholt werden, daß PAN nicht nur die dort im einzelnen untersuchten Metalle fällt, sondern noch mit zahlreichen anderen Niederschläge ergibt. Für diese weiteren Metalle wären die Bedingungen für eine quantitative Fällung von Fall zu Fall noch genau zu ermitteln sein.

Empfindlichkeit der Messung

Unter "Empfindlichkeit" sei hier die unter vorgegebenen Gerät-Parametern (Anregung, Analysatorkristall, Zähler, Zählzeit) erhältliche Intensität der Röntgenfluoreszenz je Mikrogramm Metall verstanden. Die weitverbreitete Anwendung dieses Begriffs zur Kennzeichnung der "Nachweisgrenze" ist verwirrend und metrologisch ungerechtfertigt (vgl. Ref. 19 und Fußnote in Ref. 3).

Eine spätere, genauere Untersuchung der Empfindlichkeit an zwei verschiedenen Geräten* (experimentelle Bedingungen, Geräteeinstellungen, siehe weiter unten) beruhend auf der Auswertung zahlreicher Blind- und Meßversuche ohne Metallzusatz bzw. mit je 10,0 μg des betreffenden Metalls ergab die in Tabelle I zusammengestellten Zahlenwerte.

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* Für die Durchführung dieser Messungen mit dem vollautomatischen Sequenzgerät Philips PW 1212 sind wir den Herren Dr. R. Rasin-Streden und Dr. O. Zemek der Treibacher Chemische Werke AG., Treibach, zu herzlichem Dank verpflichtet.

TABELLE 1.—EMPFINDLICHKEIT DER BESTIMMUNG VON METALLSPUREN

	Metall	Mn	Fe	Co	Ni	Cu	Zn
Philips PW 1540	Mittl.Blindwert *Imp/sec*	67	190	91	133	204	259
	Mittl.Empfindlichkeit *Imp/µg.sec*	15,2	18,8	17,9	40,0	50,2	55,3
Philips PW 1212	Mittl.Blindwert *Imp/sec*	266	711	371	489	652	728
	Mittl.Empfindlichkeit *Imp/µg.sec*	225	255	124	312	301	309

Proportionalität zwischen Metallmenge und Zählrate

Auf Grund eingehender Untersuchungen konnten wir für 0–100 µg der Metalle Mangan, Eisen, Kobalt, Nickel, Kupfer und Zink strenge Proportionalität zwischen der Netto-Impulsrate (Probe minus Blindwert) und der vorgegebenen Metallmenge feststellen; als Eichkurven erhält man Geraden.

Gegenseitige Beeinflussung der Metalle

Zu Lösungen, die je 10 µg der übrigen fünf Metalle enthielten, setzten wir 10, 20, 30, 40 und 50 µg des sechsten Metalls zu und untersuchten die mit PAN erhaltenen Niederschläge auf Abweichungen von der Empfindlichkeit, wie sie an Lösungen eines einzigen Metalls festgestellt worden war. In keinem Fall konnten wir eine signifikante, gegenseitige Beeinflussung feststellen. Dies schließt nicht aus, daß bei Vorliegen anderer Mengenverhältnisse sich gewisse Metalle gegenseitig beeinflussen können.

Richtigkeit und Reproduzierbarkeit

Über die Richtigkeit der erzielbaren Ergebnisse informiert Tabelle II.

Weitere Schlüsse auf die Richtigkeit lassen sich aus Tabelle III ableiten, wo auch die Reproduzierbarkeitsdaten zusammengefaßt sind.

Interessant schien uns ein Vergleich zwischen den in Tabelle III angeführten experimentellen Standardabweichungen s und den aus der Zählerstatistik abgeleiteten theoretischen Standardabweichungen. Letztere berechneten wir unter Berücksichtigung des Fehlerfortpflanzungsgesetzes gemäß

$$\sigma_{\text{theor}}(\mu\text{g}) = \frac{1}{\text{Empfindlichkeit } (\text{Imp}/\mu\text{g}) \cdot a} \cdot \sqrt{\frac{a \cdot (Z_p + Z_B)}{N}}$$

worin a den linearen Abschwächungsfaktor, N die Anzahl der Messungen an einer Probe, Z_P die mittlere Zähleranzeige bei Messung der Probe und Z_B die mittlere Zähleranzeige bei Messung des Blindwertes bedeuten. Eine Gegenüberstellung der s_{exp}- und σ-$_{\text{theor}}$-Werte findet sich in Tabelle IV.

Nach Durchführung des F-Tests[22] stellt man fest, daß die experimentellen Standardabweichungen im Falle von Eisen, Kobalt, Nickel, Kupfer und Zink von den theoretisch zu erwartenden signifikant ($P \geqq 99\%$) abweichen. Dies zeigt, daß außer dem Fehler bei der eigentlichen Messung im Röntgenfluoreszenzgerät weitere Fehlerquellen vorliegen (nicht streng reproduzierbare Geometrie, Einschleppung

TABELLE II.—RICHTIGKEIT DES VERFAHRENS, EINZELBESTIMMUNGEN

	Gegeben, μg	Gefunden, μg	Differenz, μg	Abweichung, %
Mangan	10,0	10,0	±0	0
	20,0	19,6	−0,4	2
	30,0	29,5	−0,5	1,7
	40,0	39,7	−0,3	0,8
	50,0	50,0	±0	0
Eisen	10,0	8,6	−1,4	14
	10,0	9,9	−0,1	1
	20,0	19,9	−0,1	0,5
	20,0	19,0	−1,0	5
	30,0	30,3	+0,3	1
	40,0	40,9	+0,9	2,2
	40,0	42,6	+2,6	6,5
	50,0	53,2	+3,2	6,4
	60,0	60,1	+0,1	0,2
Nickel	10,0	10,1	+0,1	1
	20,0	18,9	−1,1	5,5
	30,0	30,8	+0,8	2,7
	40,0	40,0	±0	0
	50,0	49,4	−0,6	1,2
Kupfer	10,0	10,2	+0,2	2
	20,0	19,0	−1,0	5
	30,0	29,6	−0,4	1,3
	40,0	42,6	+2,6	6,5
	50,0	48,7	−1,3	2,6

TABELLE III.—RICHTIGKEIT UND REPRODUZIERBARKEIT DES VERFAHRENS; MEHRFACHBESTIMMUNGEN IN GEGENWART VON JE 10 μg DER 5 ÜBRIGEN METALLE

Gegeben, μg		Anzahl der Bestimmungen	Gefunden, μg Mittelwert	Standardabweichung, μg	Variationskoeffizient, %
Mangan	10,0	7	9,91	0,13	1,3
Eisen	10,0	9	9,91	0,26	2,6
Kobalt	10,0	11	10,06	0,35	3,5
Nickel	10,0	6	10,08	0,20	2,0
Kupfer	10,0	6	10,14	0,26	2,6
Zink	10,0	6	10,08	0,21	1,2

TABELLE IV.—EXPERIMENTELLE UND THEORETISCHE STANDARDABWEICHUNG

	Mn	Fe	Co	Ni	Cu	Zn
Experimentelle Standardabweichung s_{exp}, μg	0,13	0,26	0,35	0,20	0,26	0,12
Theoretische Standardabweichung σ theor, μg	0,14	0,14	0,13	0,08	0,08	0,07
$s_{\text{exp}} > \sigma$ theor mit $P \geqslant 99\,\%$ stat. Sicherheit	nein	ja	ja	ja	ja	ja

von Spuren, Fehler bei der Fällung, Fehler bei der Filtration, Verluste bei der Manipulation).

Immerhin liegen die experimentellen Standardabweichungen außerordentlich niedrig, so daß ein Vergleich mit anderen Methoden, nach denen 10 μg eines Metalls aus 50 ml Volumen bestimmt werden können, günstig ausfällt. Tabelle IV ist auch insofern lehrreich, als man daraus ersieht, daß im allgemeinen alle übrigen Fehlerquellen größer sind, als der aus der Zählerstatistik stammende Meßfehler. Das heißt, daß die von uns vorerst willkürlich gewählte Zählzeit von 32 sec hinsichtlich der erzielbaren Reproduzierbarkeit völlig ausreicht, und daß eine Verbesserung der Reproduzierbarkeit durch Verlängerung der Zählzeit kaum sinnvoll erscheint, solange andere Fehlerursachen nicht ausgeschaltet werden können. Unseres Erachtens liegt die Hauptursache für die zusätzliche Streuung in einer ungenügenden Geometrie, d.h. das Einlegen der Filterblättchen in die Probenhalter kann nicht völlig reproduzierbar erfolgen, bzw. der Abstand Röhrenfenster–Niederschlag ist nicht völlig kontrollierbar (Wölbung des Papiers, Welligkeit der Niederschlagsoberfläche).

Erfassungsgrenze

Die Anwendung der in der qualitativen Mikroanalyse üblichen Begriffe "Erfassungsgrenze" und "Grenzkonzentration" auch zur Kennzeichnung quantitativer Mikromethoden erscheint insofern angebracht, als damit die untere Grenze der Brauchbarkeit analytischer Methoden durch objektiv bestimmbare Zahlenwerte charakterisiert werden kann.[3] Zur Berechnung dieser Kennziffern geht man zweckmäßigerweise von der allgemeinen Doerffel'schen Formulierung aus.[22] Für die Bestimmung geringer Mengen (Erfassungsgrenze) ergibt sich demnach für eine vorgegebene Zählzeit unter Annahme einer Doppelbestimmung und für eine geforderte statistische Sicherheit von 99 % folgende Formel zur Berechnung der experimentellen Erfassungsgrenze $\bar{P}_{\text{lim}}$:

$$\bar{P}_{\text{lim}}\,(\mu\text{g}) = \frac{t(P, n) \cdot s_{\text{B}}}{\text{Empfindlichkeit (Imp}/\mu\text{g)} \,.\, \sqrt{N}}$$

Hierin bedeuten: $t(P, n)$ einen Tabellenwert, abhängig von der geforderten statistischen Sicherheit P und den Freiheitsgraden n bei der Bestimmung der Schwankung des Blindwerts $s_{\bar{B}}$ und N die Anzahl der Parallelbestimmungen.

Für Mangan ergab sich beispielsweise: Blindwertmessungen = 28, daher $n = 27$; $t(99\,\%, n = 27) = 2{,}77$; Anzahl der Parallelbestimmungen $N = 2$. Alle Zählraten wurden bei 32 sec Meßzeit ermittelt. Nimmt man die τ-fache Meßzeit, so ist der Nenner mit $\sqrt{\tau}$ zu multiplizieren.

Aus 28 Blindwerten erhält man $s_{\bar{B}} = 1{,}5$ Imp/sec. Einsetzen in die Formel ergibt

$$\bar{P}_{\text{lim}}\,(\mu\text{g Mn}) = \frac{1{,}5 \cdot 2{,}77}{15{,}2 \cdot 1{,}41} = 0{,}19$$

Die solcherweise errechneten Erfassungsgrenzen für die Bestimmung von Mangan-, Eisen-, Kobalt-, Nickel-, Kupfer- und Zinkspuren in rund 50 ml wässriger Lösung sind in Tabelle V zusammengestellt.

Die experimentell ermittelten Blindwertsschwankungen liegen durchwegs höher, als die aus der Zählerstatistik errechneten Werte, somit liegen auch die experimentellen Erfassungsgrenzen höher als die theoretischen; allgemein haben wir für das Verhältnis zwischen experimenteller und theoretischer Erfassungsgrenze einen Wert

Tabelle V.—Experimentelle Erfassungsgrenze bei der Bestimmung von Metallspuren

Metall	Anzahl der Blindwerte	Erfassungsgrenze, *µg*
Mangan	28	0,19
Eisen	28	0,53
Kobalt	28	0,23
Nickel	28	0,15
Kupfer	28	0,13
Zink	28	0,12

von etwa 1,5 gefunden, im Falle des Eisens (vierthäufigstes Element auf der Erdrinde) aber rund 4.

Anwendungsmöglichkeiten

In erster Linie scheint das vorgeschlagene Verfahren zur Bestimmung von Spuren von Schwermetallionen in reinen wässrigen Lösungen, oder neben größeren Mengen von Alkali- oder Erdalkalimetallen geeignet. Schwierig und nur in Sonderfällen zu lösen dürfte die Aufgabe sein, Spuren eines Schwermetalls neben größeren Mengen eines anderen zu bestimmen, weil das PAN ein unselektives Reagens ist. In gewissen Fällen aber kann die Verwendung von Maskierungsmitteln zur Erhöhung der Selektivität führen.[20] Aussichtsreich scheint die vorgeschlagene Methode ferner noch bei der Bestimmung von Metallspuren in organischem oder biologischem Material, beispielsweise nach einem Perchlorsäure-Aufschluß. An anderer Stelle werden wir über die Bestimmung von Schwermetall-Spuren in hochreinem Molybdän und Wolfram berichten, die dadurch ermöglicht wird, daß diese beiden Metalle in Lösung anionisch vorliegen und mit dem PAN nicht reagieren. In nachstehender Tabelle VI fassen wir einige Anwendungen zusammen, die wir in letzter Zeit erfolgreich versucht haben.

Tabelle VI.—Anwendungsmöglichkeiten

Untersuchtes Material*	Einwaage	Gefundener Metallgehalt, *ppm*					
		Mn	Fe	Co	Ni	Cu	Zn
HCl conz. *p.a.*	10,0 ml	<0,02	0,06	<0,02	<0,02	<0,10	0,03
NH_3 *p.a.* "A"	10,0 ml	<0,02	<0,05	<0,02	<0,02	0,04	0,04
NH_3 *p.a.* "B"	10,0 ml	<0,02	<0,05	<0,02	<0,02	0,03	0,04
NaCl *p.a.*	1,0 g	<0,2	1,6	<0,2	<0,2	<0,1	0,6
NH_4Cl *p.a.*	1,0 g	<0,2	1,0	<0,2	<0,2	<0,1	<0,1
$K_2S_2O_7$ *p.a.*	1,0 g	<0,2	1,4	<0,2	0,2	0,2	3,4
Weinsäure *p.a.*	2,0 g	<0,1	1,3	0,1	<0,1	0,5	2,2
Methanol, techn.	1,0 ml	<0,2	3,5	<0,2	<0,2	7,3	15,7
Aceton, techn.	5,0 ml	<0,04	<0,1	<0,04	<0,04	0,1	0,08

* Die Arbeitsweise zur Spurenbestimmung ist im experimentellen Teil beschrieben.

EXPERIMENTELLER TEIL

Fällung der Metallspuren. Zu 20 bis 60 ml wässriger Lösung, die Co, Ni, Cu und Zn enthält, setzt man 5,0 ml 0,1 %-ige Lösung von PAN in *p.a.* Äthanol zu und 3 ml Puffer pH 10 (NH_4Cl-NH_3). Der Ansatz wird kurz zum Sieden erwärmt, abgekühlt und der Niederschlag wird mit Hilfe eines Filtriergerätes auf einem Scheibchen Weißband-Filterpapier mit 27 mm nutzbarem Filterdurchmesser filtriert. Filter samt Niederschlag werden bei 60° getrocknet.

Messung der Metallmengen. Das Filterpapier mit dem Niederschlag wird auf einen Standard-Probenhalter aus PVC gelegt und mit einem Blatt Mylar-Folie abgedeckt, damit der Niederschlag, der nur lose am Papier haftet, nicht bei der weiteren Manipulation herabfallen kann. Filter und Mylarfolie werden auf dem Probenträger durch Klemm- und Schraubring fixiert. Die Messung erfolgte an einem Philips-Gerät PW 1540 unter folgenden Bedingungen: Au-Röhre, 50 kV, 20 mA, Vakuum, rotierende Probe, LiF-Analysatorkristall, Scintillationszähler 900 V, Zählzeit 32 Sekunden, je 2 Messungen an der jeweiligen Kα-Linie.

Empfindlichkeit der Metallbestimmung. Philips PW 1540: Bedingungen wie oben. Philips Vollautomat PW 1212: Au-Röhre, 80 kV, 24 mA, Vakuum, rotierende Probe, LiF-Analysatorkristall, Scintillations- und Durchflußzähler gemeinsam, Zählzeit 20 Sekunden, je 5 Messungen an der Kα-Linie.

Gegenseitigte Beeinflussung. 10 μg Mn, Fe, Co, Ni, Cu, Zn gemeinsam, steigende Zusätze eines Metalls bei konstanten Mengen der übringen fünf. Messung mit Philips PW 1540.

Anwendungsmöglichkeiten. HCl conz., NH_3 conz., Methanol und Aceton wurden eingedampft, der Rückstand wurde mit 1 Tropfen HCl (1:1) aufgenommen und mit dest. Wasser auf 50 ml verdünnt. NaCl, NH_4Cl und $(NH_4)_2SO_4$ wurden in 50 ml dest. Wasser gelöst. Die Weinsäure wurde mit 7 ml conz. H_2SO_4 unter Zusatz von 1 ml Perhydrol in einem Kjeldahlkolben versacht. Die Klare Lösung wurde bis zum annähernden Trocknen abgeraucht, der Rückstand wurde mit 50 ml dest. Wasser verdünnt und mit 5 ml NH_3 conz. vorneutralisiert. Die so vorbereiteten Lösungen wurden, wie unter "Fällung der Metallspuren" und "Messung der Metallmengen" beschrieben, weiterbehandelt.

Summary—Up to 100 μg each of manganese, iron, cobalt, nickel, copper and zinc are precipitated at pH 10 by the addition of an alcoholic solution of PAN. The precipitate is collected on a filter paper, dried, and the elements determined directly by X ray fluorescence measurements. The sensitivity, accuracy and reproducibility are reported for each element. As little as 0.1–0.5 μg of each may be determined in 50 ml of solution.

Résumé—On précipite jusqu'à 100 μg de chacun des éléments manganèse, fer, cobalt, nickel, cuivre et zinc à pH 10 par l'addition d'une solution alcoolique de PAN. On recueille le précipité sur un papier filtre, le sèche et détermine directement les éléments par mesures de fluorescence aux rayons X. On rapporte les sensibilité, précision et reproductibilité pour chaque élément. On peut doser des quantités aussi faibles que 0,1–0,5 μg de chacun d'eux dans 50 ml de solution.

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METAL CHELATE EXCHANGE IN THE ORGANIC PHASE—III*

EXTRACTION AND EXCHANGE CONSTANTS OF DITHIZONATES AND OXINATES

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Summary—Reactions between dithizonates and oxinates of Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga and Bi in chloroform have been studied spectrophotometrically. From the exchange constants determined, the extraction constants of metal dithizonates or metal oxinates have been calculated. By this method extraction constants of many metal chelates can be calculated which are difficult to determine by studies of distribution between aqueous and chloroform phases.

IN PARTS I and II[1,2] the exchange reaction between metal dithizonates and diethyldithiocarbamates in the organic phase has been studied in order to find the composition and the extraction constants of metal diethyldithiocarbamates. The present paper deals with the investigation of the exchange reaction between metal dithizonates, $M(HDz)_N$, and oxine, HOx, or between metal oxinates MOx_N and dithizone H_2Dz. The exchange reaction can be generally described[1,2] by the equation

$$M(HDz)_N + N\,HOx = MOx_N + N\,H_2Dz \tag{1}$$

The exchange constant of reaction (1) is given by

$$E_{M(HDz)_N} = \frac{[MOx_N][H_2Dz]^N}{[M(HDz)_N[HOx]^N} = \frac{K_{MOx_N}}{K_{M(HDz)_N}} \tag{2}$$

where K_{MOx_N} and $K_{M(HDz)_N}$ denote the extraction constants of metal oxinates and dithizonates respectively,* and the concentrations refer to the organic phase.

Because the extraction constants of metal dithizonates are generally much higher than those of metal oxinates, it is necessary to use a great excess of oxine for the investigation of the exchange reaction (1). The exchange constants were determined by methods similar to those described previously.[1,2]

EXPERIMENTAL

Reagents

Unless otherwise stated, all reagents were of analytical reagent grade.

Chloroform. Twice distilled.

Dithizone. Purified by solvent extraction with chloroform.[3,4]

Oxine. Reagent grade, not further purified.

Metal dithizonates. Prepared as previously described.[1,2]

Metal oxinates. Solutions of metal oxinates containing excess of oxine were prepared by

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* Part II—*Talanta*, 1968, **15**, 505.

equilibrating equal volumes of an aqueous $10^{-4}M$ solution of metal ion and $0{\cdot}10M$ oxine solution in chloroform under the conditions for quantitative extraction (in the case of gallium and indium only $0{\cdot}0010M$ oxine solution was used). The organic phase was separated and filtered and the concentration of the metal oxinate determined spectrophotometrically at 380–400 nm.[3] Thallium(I) is only partially extracted by oxine solution even at high pH.[3] For this reason the concentration of thallium(I) oxinate extracted was determined (after subsequent dilution) by the exchange reaction with an excess of dithizone. The ionic strength of the aqueous solution was about 0·1 and the temperature 20–25°.

RESULTS AND DISCUSSION

Thallium

To determine the exchange constant $E_{\mathrm{TlHDz-HOx}}$, known amounts of thallium(I) dithizonate in chloroform were mixed with a known amount of oxine in the same solvent. The equilibrium concentration of thallium(I) dithizonate and dithizone was determined by the mixed colour method at 505 and 605 mm. The equilibrium concentration of thallium(I) oxinate formed is equal to the equilibrium concentration of dithizone; the concentration of oxine ($0{\cdot}1$–$0{\cdot}01M$) is practically unchanged by equilibration, for the concentration of thallium oxinate formed is $10^{-5}M$. The mean value of $\log E_{\mathrm{TlHDz-HOx}} = -5{\cdot}00 \pm 0{\cdot}04$. Practically the same value ($\log E_{\mathrm{TlHDz-HOx}} = -4{\cdot}92 \pm 0{\cdot}04$) has been found from the investigation of the exchange reaction between thallium(I) oxinate and dithizone.

If the extraction constant of thallium(I) dithizonate $\log K_{\mathrm{TlHDz}}$ is taken to be $-3{\cdot}8$,[3] the extraction constant of thallium(I) oxinate $\log K_{\mathrm{TlOx}} = -3{\cdot}8 - 4{\cdot}96 = -8{\cdot}76$. This value is in fair agreement with the value $\log K_{\mathrm{TlOx}} = -9{\cdot}5$ estimated from the work of Schweitzer and Norton.[5]

Silver

The addition of oxine ($0{\cdot}1M$ solution) to silver dithizonate in chloroform does not displace an observable amount of dithizone, *i.e.*, the exchange constant $\log E_{\mathrm{AgHDz-HOx}} \leqslant -8$.

Copper

The exchange reaction between copper dithizonate and oxine or copper oxinate and dithizone yields the same value of the exchange constant ($\log E_{\mathrm{Cu(HDz)_2-HOx}} = -7{\cdot}27 \pm 0{\cdot}03$; mean of 20 results). If the extraction constant $\log K_{\mathrm{CuOx_2}}$ is taken to be 1·40 or 1·70,[3] the extraction constant $\log K_{\mathrm{Cu(HDz)_2}} = 8{\cdot}7$–$9{\cdot}0$. The published value[3] of $\log K_{\mathrm{Cu(HDz)_2}} = 6{\cdot}5$ for chloroform seems to be too small in comparison with the value[3] 10·5 for carbon tetrachloride as a solvent. For this reason the extraction of copper ($10^{-5}M$) from $0{\cdot}05M$ sulphuric acid by dithizone solution in chloroform has been investigated. It has been found that the extraction equilibrium can be reached only after several hours' shaking. From these experiments $\log K_{\mathrm{Cu(HDz)_2}}$ (corrected for the formation of copper sulphate complexes) is 8·5, which is in agreement with the value obtained from the exchange constant.

Zinc

The results of the investigation of the exchange reaction between the zinc chelates and the organic reagents used are given in Table I. The mean value is $\log E_{\mathrm{Zn(HDz)_2-HOx}} = -7{\cdot}20 \pm 0{\cdot}02$. If $\log K_{\mathrm{Zn(HDz)_2}}$ is[3] 0·6–1·0 the value of $\log K_{\mathrm{ZnOx_2}}$ will be $-6{\cdot}2$ and $-6{\cdot}6$. From Chou's results[6] $\log K_{\mathrm{ZnOx_2}} = -6{\cdot}2$, which is in agreement with our results.

TABLE I.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{Zn(HDz)_2-HOx}$

—log of original concentration				—log of equilibrium concentration				log
[ZnOx$_2$]	[H$_2$Dz]	[Zn(HDz)$_2$]	[HOx]	[ZnOx$_2$]	[H$_2$Dz]	[Zn(HDz)$_2$]	[HOx]	$E_{Zn(HDz)_2-HOx}$
		5·04	1·70	5·50	5·20	5·22	1·70	7·28
		5·04	1·52	5·39	5·09	5·29	1·52	7·24
		5·04	1·40	5·31	5·01	5·36	1·40	7·17
		5·03	2·00	5·67	5·37	5·14	2·00	7·27
		5·03	1·70	5·50	5·20	5·22	1·70	7·28
		5·03	1·52	5·37	5·07	5·28	1·52	7·19
		5·03	1·40	5·31	5·01	5·34	1·40	7·19
		5·03	1·22	5·20	4·90	5·40	1·22	7·08
4·30	4·62		2·30	4·42	6·11	4·94	2·30	7·10
4·30	4·62		1·82	4·41	5·70	4·96	1·82	7·21
4·30	4·62		1·60	4·40	5·49	4·98	1·60	7·20
4·30	4·62		1·45	4·39	5·33	5·01	1·45	7·14
4·30	4·62		1·34	4·38	5·23	5·04	1·34	7·12
4·60	4·64		1·82	4·82	5·56	5·00	1·82	7·30
4·60	4·64		1·45	4·78	5·23	5·09	1·45	7·25
4·60	4·64		1·35	4·76	5·13	5·11	1·35	7·21
4·60	4·64		1·26	4·75	5·05	5·15	1·26	7·17
							Average =	7·20 ± 0·02

TABLE II.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{Pb(HDz)_2-HOx}$

—log of original concentration				—log of equilibrium concentration				log
[PbOx$_2$]	[H$_2$Dz]	[Pb(HDz)$_2$]	[HOx]	[PbOx$_2$]	[H$_2$Dz]	[Pb(HDz)$_2$]	[HOx]	$E_{Pb(HDz)_2-HOx}$
		4·87	2·70	5·95	5·65	4·90	2·70	6·95
		4·87	2·40	5·72	5·42	4·93	2·40	6·83
		4·87	2·30	5·68	5·38	4·94	2·30	6·90
		4·87	2·22	5·61	5·31	4·95	2·22	6·84
		4·87	2·10	5·58	5·28	4·97	2·10	6·97
		4·87	2·00	5·50	5·20	4·98	2·00	6·92
		4·87	2·00	5·52	5·22	4·99	2·00	6·97
		4·87	1·70	5·35	5·05	5·04	1·70	7·01
		4·87	1·70	5·35	5·05	5·05	1·70	7·00
		4·87	1·52	5·27	4·97	5·07	1·52	7·11
		4·87	1·52	5·28	4·97	5·08	1·52	7·10
		4·87	1·40	5·22	5·92	5·12	1·40	7·14
		4·72	2·00	5·43	5·13	4·80	2·00	6·89
		4·72	1·70	5·26	4·96	4·87	1·70	6·91
		4·72	1·40	5·12	4·82	4·94	1·40	7·02
		4·72	1·10	5·00	4·70	5·05	1·10	7·15
5·30		4·87	2·30	5·22	5·70	4·90	2·30	7·12
5·00		4·70	2·00	4·92	5·40	4·72	2·00	7·00
5·04	4·65		2·00	5·82	5·12	5·13	2·00	6·93
4·90	4·59		1·68	5·35	5·00	5·10	1·68	6·89
4·90	4·59		1·96	5·52	5·17	5·03	1·96	6·91
4·74	4·65		1·71	5·02	5·26	5·07	1·71	7·05
4·74	4·65		1·71	5·03	5·27	5·06	1·71	7·09
4·60	4·60		2·15	4·89	5·70	4·92	2·15	7·07
4·60	4·60		1·92	4·85	5·50	4·95	1·92	7·06
4·60	4·60		1·77	4·84	5·37	4·98	1·77	7·06
4·60	4·60		1·66	4·82	5·30	5·00	1·66	7·10
4·60	4·60		1·57	4·82	5·22	5·01	1·57	7·11
4·60	4·60		1·50	4·81	5·17	5·02	1·50	7·13
4·44	4·65		1·41	4·50	5·30	5·09	1·41	7·19
							Average =	7·02 ± 0·03

It is interesting to note that zinc is extracted by oxine solution as a complex of the type $ZnOx_2.2HOx$ ($\log K_{ZnOx_2.2HOx} = -2{\cdot}4$)[3] but in the exchange reaction only $ZnOx_2$ species appear to be involved, since if the experimental results are used to calculate the value of the equilibrium constant $[Zn(HOz)_2][HOx]^4/[ZnOx_2.2HOx][H_2Dz]^2$ the result $4{\cdot}04 \pm 0{\cdot}10$ is much less constant and individual values vary from 3·27 to 4·64.

Cadmium

The exchange constant for cadmium, $\log E_{Cd(HDz)_2-HOx} = 8{\cdot}48 \pm 0{\cdot}02$, has been determined in the same way as that for zinc. From the extraction constant of cadmium dithizonate ($\log K_{Cd(HDz)_2} = 0{\cdot}5$)[3] the extraction constant of cadmium oxinate ($\log K_{CdOx_2} = -8{\cdot}0$) has been calculated. This value can be difficult to determine by the conventional distribution technique because cadmium is extracted by oxine as a complex $CdOx_2.2HOx$.[3]

Lead

The mean value is $\log E_{Pb(HDz)_2-HOx} = -7{\cdot}02 \pm 0{\cdot}03$ (see Table II). This agrees well with the theoretical value ($-7{\cdot}14$) calculated from the extraction constants[3] of lead dithizonate ($\log K_{Pb(HDz)_2} = -0{\cdot}9$) and lead oxinate ($\log K_{PbOx_2} = -8{\cdot}04$).

Cobalt

From the investigation of the reaction between cobalt(II) oxinate and dithizone the value $\log E_{Co(HDz)_2-HOx} = -5{\cdot}86 \pm 0{\cdot}04$ has been determined. This value cannot be verified by the investigation of the reaction between cobalt(II) dithizonate and oxine because of the extremely slow reaction rate. The same effect has been observed in the exchange reaction between cobalt(II) dithizonate and diethyldithiocarbamic acid.[2]

Nickel

Equilibrium in the exchange reaction between nickel dithizonate and oxine or between nickel oxinate and dithizone is reached very quickly. The mean value (from 20 experiments) of $\log E_{Ni(HDz)_2-HOx}$ is $-4{\cdot}64 \pm 0{\cdot}03$. The extraction constant of nickel oxinate $\log K_{NiOx_2}$ is $-2{\cdot}18$ and therefore the extraction constant of nickel dithizonate $\log K_{Ni(HDz)_2}$ should be 2·46. The extraction constant determined by distribution between chloroform and acetate solution (concentration not stated) is $\log K_{Ni(HDz)_2} = -2{\cdot}9$.[3,4] Because of the formation of nickel acetate complexes and the very slow rate of extraction of nickel by dithizone solution in acidic medium the real value of $\log K_{Ni(HDz)_2}$ must be much higher and needs to be verified.

Palladium

The addition of oxine to palladium dithizonate solution in chloroform results in a negligible displacement of dithizone. The value $\log E_{Pd(HDz)_2-HOx}$ is < -12 and thus $\log K_{Pd(HDz)_2}$ is >27 ($\log K_{PdOx_2} \sim 15$)[3].

Indium

From the investigation of the exchange reaction between indium oxinate and dithizone or between indium dithizonate and oxine only an approximate value

$\log E_{\mathrm{In(HDz)_3-HOx}} \sim 0$ can be determined. The published data for $\log K_{\mathrm{InOx_3}}$ are 0·89 and 1·35;[3] therefore $\log K_{\mathrm{In(HDz)_3}}$ must be of the same order.

Gallium

Only the reaction between gallium oxinate and dithizone can be investigated because gallium dithizonate cannot be prepared in a pure state. The equilibrium concentration of gallium dithizonate formed was determined from the decrease of the absorption of dithizone at 505 nm. The mean value of $\log E_{\mathrm{Ga(HDz)_3-HOx}}$ is ~ 5. If the extraction constant of gallium oxinate is $\log K_{\mathrm{GaOx_3}} = 3{\cdot}72$,[3] the extraction constant of gallium dithizonate $\log K_{\mathrm{Ga(HDz)_3}}$ should be $-1{\cdot}3$ which is in agreement with extraction results.[7]

Bismuth

The mean value (20 experiments) of the exchange constant is $\log E_{\mathrm{Bi(HDz)_3-HOx}} = -9{\cdot}11 \pm 0{\cdot}04$. The value of $\log K_{\mathrm{BiOx_3}}$ is $-1{\cdot}2$,[3] and thus $\log K_{\mathrm{Bi(HDz)_3}} = 7{\cdot}9$. The two available published values, 5·2 and 8·7, differ markedly.[3,4]

CONCLUSIONS

The values of the equilibrium constants of the exchange reactions in chloroform are summarized in Table III. From the results obtained it can be seen that the equilibrium constants can be accurately determined. Equilibrium is reached very quickly and in most cases the exchange reactions are completely reversible, *i.e.*, the same value of the exchange constant is obtained by the investigation of the reaction between metal dithizonate and oxine or between metal oxinate and dithizone.

TABLE III.—EQUILIBRIUM CONSTANTS OF EXCHANGE REACTION, E, AND EXTRACTION CONSTANTS OF METAL DITHIZONATES, $K_{\mathrm{M(HDz)}_N}$ AND OF OXINATES, K_{MOx_N}

Reaction	log E*	log $K_{\mathrm{M(HDz)}_N}$	log K_{MOx_N}
$\mathrm{TlHDz + HOx = TlOx + H_2Dz}$	$-4{\cdot}96 \pm 0{\cdot}04$	$(-3{\cdot}8)^{3,4}$	$-8{\cdot}76$
$\mathrm{AgHDz + HOx = AgOx + H_2Dz}$	$\leqslant -8$		
$\mathrm{Cu(HDz)_2 + 2HOx = CuOx_2 + 2H_2Dz}$	$-7{\cdot}27 \pm 0{\cdot}03$	8·7–9·0	$(1{\cdot}4\text{–}1{\cdot}7)^3$
$\mathrm{Zn(HDz)_2 + 2HOx = ZnOx_2 + 2H_2Dz}$	$-7{\cdot}20 \pm 0{\cdot}02$	$(0{\cdot}6\text{–}1{\cdot}0)^3$	$-(6{\cdot}2\text{–}6{\cdot}6)$
$\mathrm{Cd(HDz)_2 + 2HOx = CdOx_2 + 2H_2Dz}$	$-8{\cdot}48 \pm 0{\cdot}02$	$(0{\cdot}5)^{3,4}$	$-8{\cdot}0$
$\mathrm{Hg(HDz)_2 + 2HOx = HgOx_2 + 2H_2Dz}$	$\leqslant -14$		
$\mathrm{Pb(HDz)_2 + 2HOx = PbOx_2 + 2H_2Dz}$	$-7{\cdot}02 \pm 0{\cdot}03$	$-1{\cdot}02$	$(-8{\cdot}04)^3$
$\mathrm{Co(HDz)_2 + 2HOx = CoOx_2 + 2H_2Dz}$	$-5{\cdot}86 \pm 0{\cdot}04$		
$\mathrm{Ni(HDz)_2 + 2HOx = NiOx_2 + 2H_2Dz}$	$-4{\cdot}64 \pm 0{\cdot}03$	2·46	$(-2{\cdot}18)^3$
$\mathrm{Pd(HDz)_2 + 2HOx = PdOx_2 + 2H_2Dz}$	< -12	> 27	$(15)^3$
$\mathrm{In(HDz)_3 + 3HOx = InOx_3 + 3H_2Dz}$	~ 0	~ 1	$(0{\cdot}9\text{–}1{\cdot}3)^3$
$\mathrm{Ga(HDz)_3 + 3HOx = GaOx_3 + 3H_2Dz}$	~ 5	$\sim -1{\cdot}3$	$(3{\cdot}72)^3$
$\mathrm{Bi(HDz)_3 + 3HOx = BiOx_3 + 3H_2Dz}$	$-9{\cdot}11 \pm 0{\cdot}04$	7·9	$(-1{\cdot}2)^3$

* The errors quoted are the standard errors of the means.

The value $1/N \log E_{\mathrm{M(HDz)}_N-\mathrm{HOx}}$ measures the relative affinity of the chelating agents for the metal investigated. Metals with a positive value for $1/N \log E_{\mathrm{M(HDz)}_N-\mathrm{HOx}}$ have a greater higher affinity for oxine than dithizone (*e.g.*, gallium); a negative value denotes the affinity is higher towards dithizone (*e.g.*, mercury, silver).

When the extraction constant of one metal chelate (dithizonate or oxinate) is known the extraction constant of the second metal chelate can be readily calculated even when conventional distribution measurements cannot be used because of hydrolysis or complexation in the aqueous phase, decomposition of the reagent or the chelate formed, or slowness of equilibration. Thus in the present paper the extraction constants of dithizonates of copper, lead, nickel, indium, gallium and bismuth and the extraction constants of oxinates of thallium(I), zinc and cadmium have been determined. There was no evidence of the formation of the mixed type of complex, M(Ox)(HDz).

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Zusammenfassung—Die Reaktion zwischen Dithizonaten und Oxinaten von Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga und Bi in Chloroform wurden spektrophotometrisch untersucht. Aus den ermittelten Austauschkonstanten wurden die Extraktionskonstanten der Metalldithizonate bzw. -oxinate berechnet. Auf diese Weise kann man Extraktionskonstanten vieler Metallchelate berechnen, die durch Untersuchung der Verteilung zwischen wäßriger und Chloroformphase schwierig zu bestimmen sind.

Résumé—On a étudié spectrophotométriquement les réactions entre les dithizonates et les oxinates de Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga et Bi en chloroforme. Des constantes d'échange déterminées, on a calculé les constantes d'extraction des dithizonates ou oxinates métalliques. Par cette méthode, on peut calculer les constantes d'extraction de nombreux chélates métalliques qu'il est difficile de déterminer par des études de partage entre phases aqueuse et chloroformique.

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AN ELECTRICAL DETECTION SYSTEM FOR A SPARK-SOURCE MASS SPECTROGRAPH*

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Summary—An electrical detection system has been developed which can be used with the high-frequency spark-source mass spectrograph. Details of the system are discussed and examples are given illustrating its advantages (rapidity and precision). One distinct advantage of electrical detection is that a constant volume of sample material is used for each impurity determination. The system can also be used to assess sample inhomogeneities.

THE ion-sensitive photoplate is the traditional detection method used in spark-source mass spectrography. The efforts made to solve some of the problems attending its use have been discussed by Ahearn.[1] Although the photoplate is ideally suited for detecting large numbers of impurities in a sample, it's use is awkward when only a limited number of impurities are of concern to the analyst. In addition, there are time-consuming steps involved in handling photoplates and photoplate data, and sample inhomogeneities disturb the results. An electrical detection system for the spark-source instrument should greatly shorten the time required to collect both qualitative and quantitative analytical results and greatly simplify the data reduction required to produce an analytical report. At the same time it might be useful for determining directly the degree of inhomogeneity in samples. With these considerations in mind, the development of the electrical detection system described here was initiated.

To date no wholly satisfactory electrical detection system has been developed for the spark-source mass spectrograph. Strauss[2] made the first serious attempt to apply electrical detection to spark-source ion-currents from the nickel isotopes. Ten years later, in 1951, Gorman, Hipple and Jones[3] introduced the use of the ion "beam monitor" in an assay of the major components in several steels. In 1961, Chakravarty, Venkatasubramanian and Duckworth[4] extended this method in a determination of some sensitivity factors and Fluegge[5] obtained a spark-source spectrum of silicon in a time-of-flight mass spectrometer. Dörnenburg and Hintenburger[6] attempted to use electrical detection as an aid in determining photoplate sensitivities. In 1964, Dupzyk, Barton, Carver and Thomas[7] described a time-averaging scheme to enhance signal-to-noise ratios in electrical data, and in 1965, Conzemius, Capellen and Svec[8] compared the results of electrical and photographic measurements made on eight NBS low-alloy steels. In 1967, Svec and Conzemius[9] described some preliminary results with an electrical system capable of peak-scanning. Bingham and Powers[10] in 1968 discussed electrical detection methods for improving

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quantitative analyses and Hull[11] discussed the sensitivity, accuracy and speed attending its use in spark-source mass spectrography.

The electrical detection system described below combines the best features of some of the foregoing methods, augmented by up-to-date electronic technology. The system accommodates to electrical noise, interrupted ion-beams, fluctuating ion-beams, variable sparking conditions, energy spread of the ions in the beam and spark duty cycles. It has a dynamic range of 7–8 orders of magnitude and provides for peak resolution and identification. Mass scanning is convenient, simple and reliable. The results are displayed digitally thereby affording the operator immediate information concerning the measurements and at the same time the instrument is amenable to computer control and interpretation. The spark source instrument (Nuclide-Graf 2.2) has been retained so that photographic usage is possible as an alternative. Components have been selected which make it possible to incorporate rapid data acquisition equipment and computer interfacing equipment so that additional development, if necessary, can be achieved with ease.

APPARATUS

The physical arrangement of the mass spectrograph is shown in Fig. 1. The position of a special slit-containing plate which takes the place of the normal photographic plate is shown. The size of the slit shown in this figure is that used in previous electrical detection work[8] and has been changed subsequently to improve the mass resolution. The "screen monitor" has been removed and replaced by two Z-limiting plates and provisions have been made to eliminate problems due to secondary electron emission caused by ion bombardment of these and other electrodes and grounded apertures near the monitor. Faraday cup collectors may be positioned to intercept the ion-beam at the monitor and/or in front of the first dynode of a 20-stage electron-multiplier. Thus it is possible to monitor the ion-beam periodically in order to check on alignments in the ion-optics system and on the collection efficiency for the principal ion-beams. Although the results presented later are based on measuring the ratio of a particular ion-current at the collector to that at the monitor, a second multicollector holder has been designed and built which makes it possible to measure the ratio of a particular ion-current to that of the matrix. This enables the analyst to use as an internal standard one of the lines from the matrix or any other substance present in the sample.

Previous experience[8] with a much more cumbersome electrical detection system indicated it was possible to obtain an average analytical precision of about ±6% for 14 impurities in eight low alloy steels covering a concentration range from 10 ppm to 1·73%. No deterioration of the precision was

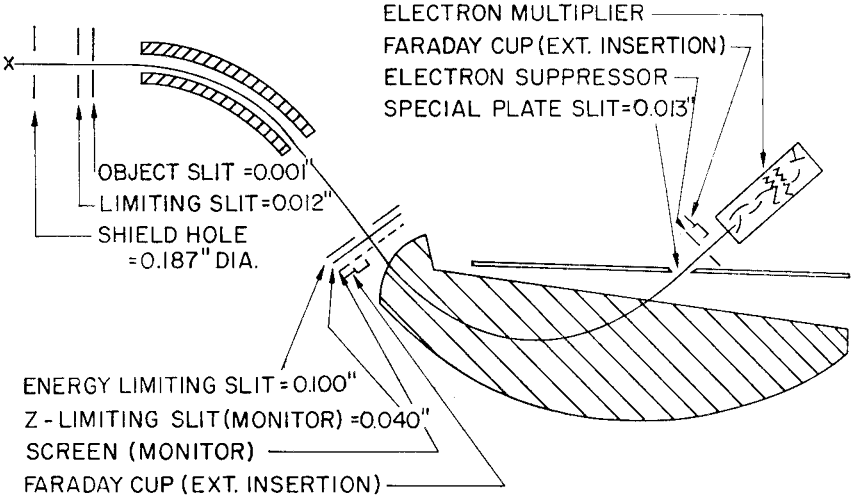

Fig. 1.—Apertures and ion-detectors for the electrical detection system.

observed at the lower concentrations. All the results were obtained by using the same volume of sample (3·3 × 10^{-13} m^3) for each determination regardless of concentration level. This volume of material corresponded to ~39,000 sample grains, with an average of 5 inclusions per impurity. It was 5 times the minimum amount of sample recommended by the NBS for optical spectrographic use. Figure 2 summarizes the precision of all the electrical readings taken during the experiments regardless of what impurity element was being considered. Note that although the average precision obtained throughout is ±6%, many of the measurements (62 of the 99) were made with precisions appreciably better. Considering that these results include possible variations in the NBS certified values and that 16 of the 90 certified values used contain only *one* significant figure, the prospects for electrical detection were encouraging. Two distinct advantages inherent in electrical detection were apparent; *the volume of sample is the same for all impurity levels* and the time required to obtain reliable analytical results is very short compared with that for photographic methods.

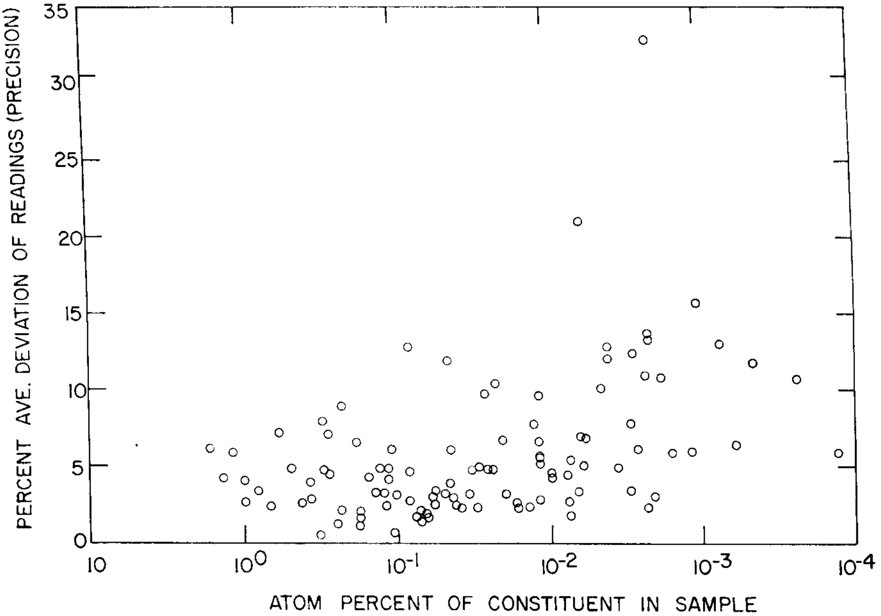

FIG. 2.—Precision of electrical analyses.

The new electrical detection system is shown in block diagram in Fig. 3. For the present the monitor and a single collector after magnetic separation are still being used to obtain ratios used in analytical applications and only limited experience has been gained with the multicollector electrode. The currents at the monitor and single collector are amplified and the resultant voltages converted into frequencies which are compared in a ratio meter. For very low impurity concentrations, ion-counting can be used *via* the pulse amplifier, and counting-rates compared directly with the counts from the monitor VFC. The output of the ratio meter is recorded by the printer. (A tape punch could also be used.) The printer controls a step scanning circuit which is activated only when a preselected number of counts is accumulated in the "denominator" channel of the ratio meter. Thus if the spark shuts off for any reason, scanning does not proceed until the spark is restarted, thereby eliminating gaps in a recorded mass spectrum. The components and more details of the system are shown in Fig. 4. The ion-detector may be a Faraday cup or a 20-stage electron-multiplier. Although the figure indicates the use of Cary Model 31 vibrating reed electrometers as current amplifiers, wider band amplifiers (Keithley 601A electrometers) and fast amplifiers (Fairchild, Model ADO-26B) have also been used. The various results indicate that current amplification is not a serious problem, but rather that other conditions such as changes in sparking position and sample inhomogeneities may limit the ultimate analytical precision obtainable.

The amplifier outputs are coupled to 0–1-V input, 0–100-kHz frequency converters (Dymec, Model 2211BR). The output of the electron-multiplier can alternatively be connected to a pulse amplifier (Baird Atomic 215) for operation in the direct counting mode. The output of the pulse amplifier or converter provides the numerator for the digital ratio meter (Hewlett-Packard, Model 5245L, 50 MHz count rate) with the denominator coming from the monitor converter. Recording of

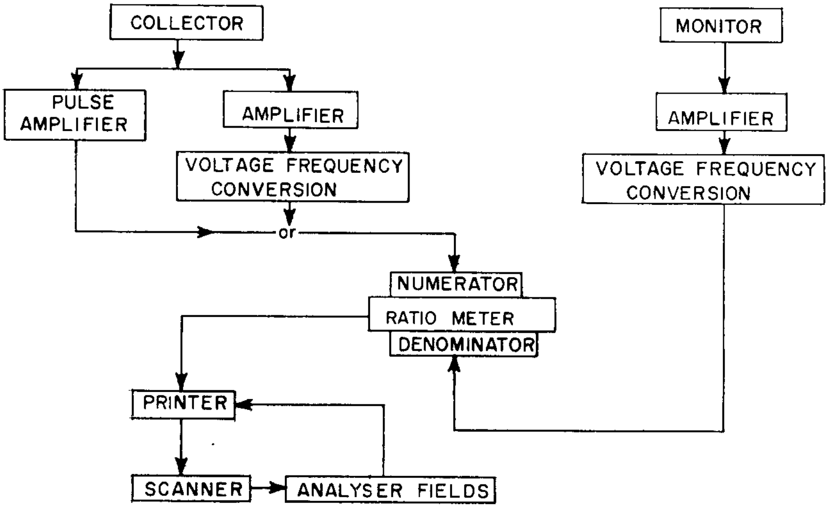

Fig. 3.—Block diagram of electrical detection system.

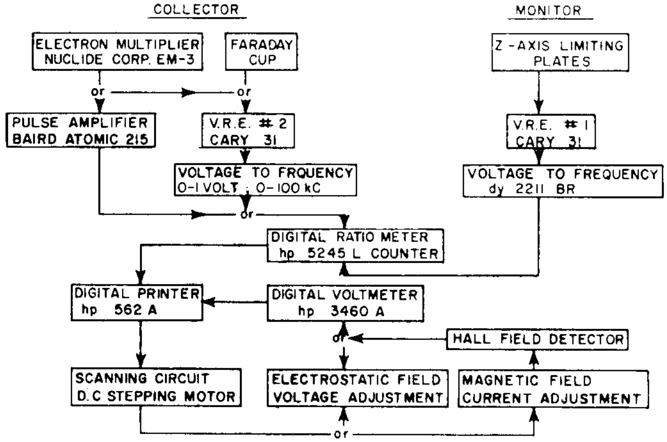

Fig. 4.—Components of electrical detection system. Vibrating reed electrometer amplifiers have been replaced by fast wide-band amplifiers.

the ratio and of the mass indicator is performed with a digital printer (Hewlett-Packard, Model 562A) which provides a total of 11 characters for two independent and parallel entries with a printing cycle of 200 msec. The mass indicator is a digital voltmeter which has a 10-μV sensitivity and a 5-digit read-out. This indicator measures a fixed fraction of the ion-accelerating electrical field when electrostatic scanning is utilized or measures the output of a Hall-crystal detector when magnetic scanning is used.

Automatic stepwise scanning is achieved in a step-by-step control of the measuring cycle. By controlling the gate opening of the ratio meter and each step of the staircase scan, no portion of the spectrum is missed. Figure 5 shows the measuring cycle. The counter gate of the ratio meter is open to accept a preset number of counts from the monitor VFC, usually 10,000 counts. The digital voltmeter gate is also open but for a preset time of 0·1 sec or less. When the voltmeter and counter gates close, print commands are given and the counter and voltmeter are inhibited from accepting any signals. The printer is delayed for ~2 msec after the second print command and then begins its printing operation during which the output of the ratio meter and digital voltmeter are recorded. Also at the time of the second print command a scan command is given and scanning takes place.

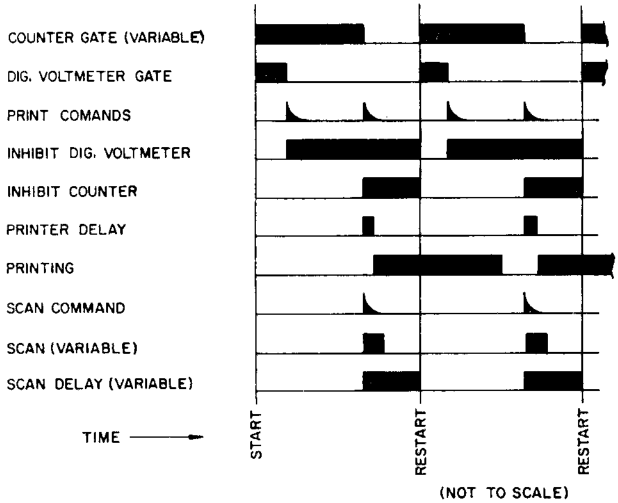

Fig. 5.—Measuring cycle for the electrical detection system.

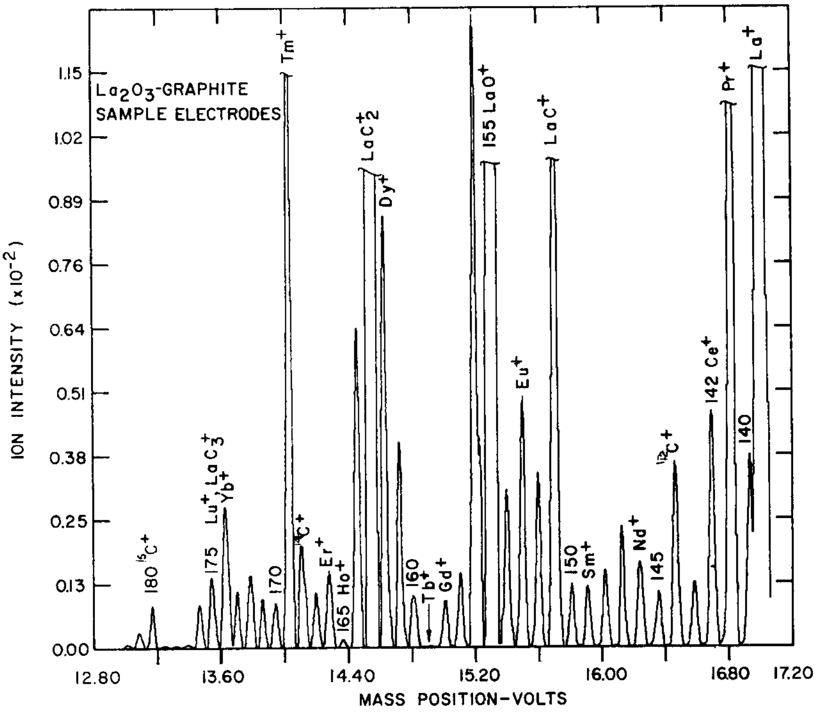

Fig. 6.—A computer plot of the data from a stepwise scan through the rare earth mass region for a lanthanum oxide sample which has been pelleted with graphite. This plot is at 10× the base sensitivity.

(The stepwise change of the scanning field requires 0·1 sec or less.) A variable scan delay is operative to allow sufficient time for the field being adjusted to settle and to ensure that the voltmeter and counter inhibition is maintained until everything is ready for the cycle to be repeated. The cycle restarts by opening the measuring gates. The automatic scanning feature of the system can be deactivated and replaced by a manual peak-switching circuit which uses a keyboard-actuated, relay-operated voltage divider to adjust the circuit involved with the appropriate scanning field. Thus the entire system can be operated so as to scan a mass spectrum continuously or to switch from peak to peak associated with particular impurities of interest to the analyst. An example of an actual computer-plotted scan (data taken from the printed tape) for this system in the automatic scan mode is shown in Fig. 6. This is an ion-accelerating voltage scan of the rare earth mass region of a lanthanum oxide sample doped with other rare earths. An initial plot is usually scaled to set the maximum peak at full scale. Additional plots are then made at sensitivity increases of 10 ×.

RESULTS AND DISCUSSION

In order to establish guide lines for operating conditions with the electrical detection system, a series of experiments was performed with NBS Steel Standard 461 which has been studied metallographically and certified for homogeneity.[12] Four series of observations were made, based on ratios obtained from single observations involving 1, 10, 100 and 1000 spark pulses, corresponding to sparking times of 0·01, 0·1, 1·0 and 10 sec each. From 10 to 40 observations were made in each series. The results for six of the alloying elements in the steel and two iron isotopes are summarized in columns five and six of Table I. As was expected, the precision of the series involving 1000 spark pulses per observation was best but that obtained with only 100 or even 10 pulses is acceptable. The results also indicate that the precision attending single pulse observations is as good or better than the best expected from photographic detection.

The results shown are a good representation of the reproducibility for small aliquots of homogeneous sample material and are not integrated values dependent on a long amplifier time-constant. The results are promising and indicate what can be expected in terms of speed as well as reproducibility. They also indicate potential use in inhomogeneity studies.

The ^{57}Fe/^{54}Fe ratio from these results is 0·386 when the means of the series means are used to calculate the value. This may be compared with the four most recently published[13–16] measurements of this ratio, ranging from 0·367 to 0·380. It thus appears that the electrical detection system would be reasonably accurate.

As a further test, a sample of erbium metal was analysed electrometrically for La, Ce, Pr and Nd with manual peak-switching. All ratios of collector current to that of the monitor were referred to the ratio of ^{162}Er$^+$/monitor, which was measured regularly as an internal standard. Results were obtained on three different days as listed in Table II. Each single determination (*e.g.*, 15·5 ± 0·5 ppma for La on 19 Feb.) consisted of a series of 5 observations 1–2 sec long. Corrections were made for the background, which was measured at various points in the mass range of interest. To find whether gross changes in the analytical results occurred because of changes in sparking conditions and/or ion transmission through the instrument, ratios of the ion-currents ^{162}Er$^+$ and ^{164}Er$^+$ to that of the monitor were measured each time the spark geometry was visually observed to change or when erratic signals were obtained. Apparent elemental concentrations were calculated from the measured ratios, only the isotopic correction being considered and unit relative gain being assumed for the multiplier. All determinations were obtained by a similar treatment but the results were treated independently. All observations were made with a duty cycle of 32

TABLE I.—ION-CURRENT RATIOS, NBS STEEL 461, M^+/MONITOR CURRENT

Element	Conc., *ppma**	Isotope	Series†	Means of series	Relative std. devn. of mean, %	Mean of means‡	Relative std. devn. of mean of means, %
Vanadium	260	^{51}V	1	0·0149	0·6		
			2	0·0156	1·4		
			3	0·0151	2·7		
			4	0·0149	7·0	0·0151	0·9
Chromium	1390	^{52}Cr	1	0·0719	0·4		
			2	0·0802	0·7		
			3	0·0725	1·6		
			4	0·0760	5·0	0·0751	2·1
Cobalt	2460	^{59}Co	1	0·0908	0·5		
			2	0·0883	0·5		
			3	0·0903	1·9		
			4	0·0862	5·9	0·0890	1·1
Copper	2990	^{63}Cu	1	0·0967	0·6		
			2	0·1019	0·9		
			3	0·1034	2·7		
			4	0·1087	7·9	0·1026	2·1
Manganese	3660	^{55}Mn	1	0·2802	0·6		
			2	0·2709	0·6		
			3	0·2677	1·5		
			4	0·3117	4·2	0·2826	3·1
Nickel	16460	^{60}Ni	1	0·1159	1·3		
			2	0·1246	0·9		
			3	0·1245	1·9		
			4	0·1143	6·2	0·1198	2·0
Iron	matrix	^{57}Fe	1	0·8583	0·2		
			2	0·8754	0·7		
			3	0·8623	1·3		
			4	0·8730	4·8	0·8672	0·4
Iron	matrix	^{54}Fe	1	2·2107	0·3		
			2	2·2027	0·4		
			3	2·1822	1·2		
			4	2·3740	5·1	2·2422	1·7

* ppma = atoms per million atoms (parts per million, atomic).

† Series 1; 10 measurements, 10 sec each; series 2, 3, 4, 25–40 measurements, 1, 0·1 and 0·01 sec each, respectively.

‡ Conversion of these values into concentrations (in ppma) requires application of isotope abundance factors as well as relative sensitivity factors.

spark pulses per sec with a pulse length of 32 μsec. The multiplier gain was approximately 10^6 and electrostatic scanning (between 20 and 15 kV) was used. Analysis of the same sample by photographic detection was performed immediately after the electrometric experiments. The photographic data were treated according to the method of Owens and Giardino[17] with corrections made for isotopic abundance, line width, mass response and background. The constant value for the ratio of the results obtained by the two methods indicates that both detection systems were working well, and the difference from unity probably means that the treatments of the electrical and/or the photographic data do not introduce the same bias into the results. Presumably this difference would disappear if proper sensitivity factors based on standards were used in both cases. The entire group of electrometric measurements on this sample have been repeated subsequently many times as a check on the reproducibility of results over an extended period. The results for La, Ce, Pr and Nd are essentially the same as given in the table. In addition, other rare earth impurities have been determined. The electrometric results are Eu 0·09 ± 0·005, Sm 0·19 ± 0·02, Gd 14·8 ± 0·8, Tb 1·1 ± 0·06, Dy 3·4 ± 0·3, Lu 1·3 ± 0·06, and Pb 8·8 ± 0·09 ppma. The comparable figures for photographic detection are: Eu $< 0·3$, Sm $< 0·1$, Gd 13·2; Tb 0·9, Dy 3·7 and Lu 2·1 (no value was measured for Pb). In the case of Lu, the photographic value is probably high because a sample of Lu was the previous material in the instrument. The electrical/photographic ratios in these cases are not the same as for the four elements in Table II. This is probably because of the greater number of interferences and the value of the background correction in the mass range involved. The electrical results indicate that gadolinium is not homogeneously distributed in the sample. In the case of dysprosium, the electrical/photographic ratio is less than unity. However, no reliable value for the background in the Dy mass region was obtainable and the raw data could have been overcorrected for background.

The overall results indicate that the precision of the electrical measurements ranged from approximately 1 to 10% over a range of four orders of magnitude in the concentration of impurities. The time required to obtain useful analytical data is short with the electrical detection system. For example, all the data necessary to characterize all of the rare earth and some of the common impurities in the erbium sample were obtained in approximately 10 min. The data, however, were immediately available for computing the analytical results. Comparable instrument time for photographic detection is 1 hr. In addition, time must be allowed for retrieval of the plate, development, emulsion calibration and microdensitometry before the data are in a form which can be used to compute the analytical results.

Another test of the electrical detection system was performed with a sample of scandium oxide which had been doped with rare earth oxides at levels between 250 and 400 ppma. Indium oxide was added as an internal standard. Mechanical mixing in an alundum capsule was used to blend the various oxides.[18] The resulting mixture was further mixed with graphite (2 moles of graphite to 1 mole of oxide) and pressed into a pellet, polyethylene film being used as an interface between the mixture and the pellet die. The pellet was cut in half and the two sections sparked against each other under the same conditions as for the erbium metal. The oxide data were treated the same as the metal data except that the analytical results were normalized to the internal standard indium. In terms of analytical reproducibility this pellet is a non-homogenous sample although it is quite thoroughly blended. The same pellet was also analysed with photographic detection *etc.* and the indium internal standard. Two series of electrical measurements and three independent photographic determinations were made. A summary of the results is given in Table III. All uncertainties cited are average deviations except in cases where only a single measurement was available. The ratio of the electrical/photographic relative sensitivity factors should be unity if there is no systematic bias between the two methods of detection. As shown in column 8, this ratio has a value less than one for all cases except Ce and Pr. This is to be expected since no correction for multiplier efficiency as a function of ion energy was applied to the electrical data. Since electrostatic mass scanning was employed in these measurements the ion energy and mass correction would tend to increase the value of all electrical detection results. However, the wisdom of applying

TABLE II.—ELECTROMETRIC AND PHOTOGRAPHIC DETERMINATION OF SOME RARE EARTHS IN ERBIUM METAL*

		Electrical detection results									
		19 Feb. 68			20 Feb. 68	21 Feb. 68					Ratio
Element	Isotope	1	2	3	1	1	2	3	Average, 7 runs†	Photographic results	electrometric / photographic
La	139	15·5±0·5	14·9±0·6	15·6±0·7	15·3±0·4	14·5±0·4	13·0±0·4	12·7±0·2	14·5±1·2	7·6	1·91
Ce	140	3·2±0·1	3·4±0·2	3·2±0·1	3·5±0·1	3·1±0·2	2·6±0·1	3·0±0·2	3·2±0·2	1·7	1·88
Pr	141	9·9±0·3	9·7±0·3	9·3±0·3	9·2±0·2	8·7±0·3	8·4±0·5	8·1±0·3	9·0±0·7	4·8	1·88
Nd	143	6·4±0·5	3·8±0·7	5·4±0·6	8·2±0·2	6·6±0·8	7·3±0·2	5·0±0·3	6·1±1·5	3·2	1·91

* Values are given in ppma, uncertainties are standard deviations of single observations in each series of five observations.

† Standard deviation of the average for the seven runs.

TABLE III.—ELECTROMETRIC AND PHOTOGRAPHIC DETERMINATION OF RARE EARTHS IN SCANDIUM OXIDE

Element	Isotope	Nominal conc., *ppma*	Elect.*	Photog.†	Observed value/nominal value		Ratio elect./photog.	Ratio‡ elect./photog.
					elect.	photog.		
La	139	298	229	207±15	0·77	0·69±0·05	1·12	1·23
Ce	140	371	198±13	175±26	0·53±0·04	0·47±0·07	1·13	1·23
Pr	141	295	214±38	261±10	0·73±0·13	0·88±0·03	0·82	0·92
Nd	146	304	216±21	244±19	0·71±0·10	0·80±0·06	0·89	0·99
Sm	149	278	250±26	317±19	0·90±0·09	1·41±0·07	0·80	1·01
Gd	157	330	234±34	319±48	0·71±0·10	0·97±0·15	0·73	0·86
Tb	159	295	153±15	179±20	0·52±0·05	0·61±0·07	0·85	1·00
Dy	161	331	250± 9	269±24	0·76±0·03	0·81±0·07	0·94	1·10
Ho	165	258	184	196±17	0·71	0·75±0·07	0·93	1·13
Tm	169	396	258±44	326±45	0·65±0·11	0·82±0·11	0·79	0·96
Yb	174	260	178± 7	271±10	0·68±0·03	1·04±0·04	0·65	0·81
Lu	175	283	90± 3	138±16	0·32±0·01	0·49±0·06	0·65	0·80
						Ave.	0·86	1·01

* Two series of 5 observations were made; the average deviations are shown.

† Three different photoplates were used; average deviations are shown.

‡ Correction applied to electrometric results, see text.

such a correction at present is questionable because of the lack of definitive information concerning the exact mathematical form in which it should be applied and the inter-relationship of indium as an internal standard. Also, although indium has been used extensively as an internal standard in our laboratory for rare earth assays, recent unfinished critical evaluations of its general applicability have introduced some doubt in our minds concerning its value. However, a correction factor based simply on the square root of the ratio of rare earth nuclide mass/^{115}In was applied to the electrometric data and the same ratios, electrometric/photographic, were recomputed. The results are shown in column 9. Generally the agreement between the two methods is improved, especially considering the uncertainty due to the inhomogeneity of the pellets and to choice of correction for multiplier response. Perhaps the ultimate improvement in the reliable use of this electrical detection system will come when more experience has been gained with ion-counting methods which will obviate problems due to electron-multiplier gain. It is clear, however, that electrical detection methods greatly shorten the time required to obtain good spark source analytical data and the expected precision of the results from homogeneous samples is very good. Even with inhomogeneous samples such as graphite–oxide mixes, the use of small sample volumes for each impurity observation does not introduce uncertainties greater than those of photographic detection used with the same type of sample.

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Zusammenfassung—Ein elektrisches Nachweissystem für den Massenspektrographen mit Hochfrequenzfunken-Quelle wurde entwickelt. Einzelheiten des Systems werden diskutiert und Beispiele angegeben, die seine Vorteile zeigen (Schnelligkeit und Genauigkeit). Ein besonderer Vorteil des elektrischen Nachweises ist, daß ein konstantes Probenvolumen für die Bestimmung jeder Verunreinigung gebraucht wird. Das System kann auch zur Ermittlung von Inhomogenitäten in der Prode verwendet werden.

Résumé—On a élaboré un système de détection électrique qui peut être utilisé avec le spectrographe de masse à source d'étincelle haute fréquence. On discute des détails du système et donne des exemples illustrant ses avantages (rapidité et précision). Un avantage marqué de la détection électrique est qu'on utilise un volume constant de substance échantillon pour chaque détermination d'impureté. On peut aussi utiliser le système pour apprécier les hétérogénéités de l'échantillon.

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CATION-EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN HYDROBROMIC ACID–ORGANIC SOLVENT MEDIA

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Summary—The cation–exchange characteristics of 19 elements in hydrobromic acid–organic solvent media have been investigated. In these systems the batch distribution coefficients of the metal ions were determined, using the strongly acidic cation-exchange resin Dowex 50, X8. Methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran and acetic acid have been used as the organic solvents. The conditions most suitable for the quantitative separation of the elements are indicated and discussed. Several examples of successful separations are tabulated.

A systematic investigation of the adsorption behaviour of numerous metal ions on Dowex 50, X4 in pure aqueous hydrobromic acid solutions of varying concentrations has recently been performed.[1] As a result several useful cation-exchange separations of elements can be achieved.

On the other hand no attempt has so far been made to investigate systematically the broad field of mixed aqueous–organic solvent media, containing hydrobromic acid, with respect to their applicability to cation-exchange separations. To obtain a complete picture of the adsorption characteristics of the elements, the research work presented in this paper was performed, using the most frequently employed cation-exchange resin Dowex 50 in mixtures of 8 organic solvents containing hydrobromic acid. For this purpose the same variables, *i.e.*, concentration of organic solvent and concentration of mineral acid, have been investigated as in previous publications dealing with cation-exchange behaviour in hydrochloric,[2] nitric[3] and hydrofluoric[4] acid media containing the same organic solvents. Consequently the results for all the systems are readily comparable.

EXPERIMENTAL

Reagents

Ion-exchange resin. The air-dried strongly acidic cation-exchanger Dowex 50, X8(100-200 mesh, hydrogen form) was used for the batch and separation experiments.

Standard solutions. Exactly weighed amounts of UO_2(II), Th(IV), Ce(III), Mo(VI), V(V),* Fe(III), Al(III), In(III), Bi(III), Mg(II), Ca(II), Sr(II), Pb(II), Zn(II), Cd(II), Cu(II), Mn(II), Co(II) and Ni(II) as bromides, oxides, carbonates or hydroxides were dissolved in 6*M* or 9*M* hydrobromic acid to give solutions containing 5 or 10 mg of the element/ml.

Solvents. The reagent-grade pure organic solvents used were methanol, ethanol, n-propanol, isopropanol, methyl glycol (monomethyl ether of ethylene glycol, CH_3—O—CH_2—CH_2OH), glacial acetic acid, tetrahydrofuran and acetone.

* In the presence of bromide and organic solvents vanadium is readily reduced to the quadrivalent state.

Determination of the various elements

Most of the elements investigated were determined titrimetrically, by suitable chelatometric methods with EDTA (disodium salt) as the titrant. Molybdenum was determined by titration with standard lead nitrate solution.[4]

Determination of distribution coefficients

The weight distribution coefficients (K_d values) of all elements were determined by using the batch equilibrium method (batch method) described in earlier publications.[2,3]

RESULTS AND DISCUSSION

In Tables I–XVII the metal ions are arranged in the same order. The solubilities of lead bromide in some hydrobromic acid–acetic acid mixtures and of copper bromide in very dilute pure aqueous hydrobromic acid were found to be very low, so a determination of the distribution coefficients in these media was not possible. In these instances the Tables do not list the distribution coefficients, instead the abbreviation "ppt" (for precipitation) has been used.

Aliphatic alcohol media

In Tables I–IV and IX–XII, the distribution coefficients measured in hydrobromic acid-aliphatic alcohol mixtures (methanol, ethanol, n-propanol and isopropanol) are shown.

TABLE I.—DISTRIBUTION COEFFICIENTS IN AQUEOUS METHANOLIC 0·6*M* HYDROBROMIC ACID

Ion	Methanol concentration, %					
	0	20	40	60	80	90
UO$_2$(II)	75	100	220	$>10^3$	$>10^3$	600
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	5	5	6	7	23
V(IV)	22	24	34	56	70	106
Fe(III)	430	500	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	10	8	6	1	<1
Bi(III)	3	1	<1	<1	<1	<1
Mg(II)	36	35	58	98	150	170
Ca(II)	90	130	250	$>10^3$	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	31	19	15	5	1
Zn(II)	55	68	82	65	9	<1
Cd(II)	2	<1	<1	<1	<1	<1
Cu(II)	50	70	100	102	102	30
Mn(II)	50	63	95	260	450	500
Co(II)	62	78	120	310	410	290
Ni(II)	70	85	150	450	800	300

Uranium(VI), thorium(IV) and cerium(III). Thorium and cerium show the same distribution coefficient of $>10^3$ at all concentrations of aliphatic alcohols and hydrobromic acid. On the other hand the adsorption of uranium is frequently lower than that of thorium or cerium especially at low concentrations of aliphatic alcohols and at high concentrations of hydrobromic acid in the presence of methanol or n-propanol. However, under these conditions the distribution coefficients of uranium are still too high to allow its successful separation from thorium and cerium. Consequently these

TABLE II.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ETHANOLIC 0·6*M* HYDROBROMIC ACID

Ion	Ethanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	75	140	400	$>10^3$	$>10^3$	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	7	8	8	11	16
V(IV)	22	27	44	95	230	380
Fe(III)	430	900	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	13	12	10	3	<1
Bi(III)	3	3	2	2	<1	<1
Mg(II)	36	34	67	75	240	$>10^3$
Ca(II)	90	140	630	$>10^3$	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	34	25	19	7	2
Zn(II)	55	71	110	90	10	<1
Cd(II)	2	<1	<1	<1	<1	<1
Cu(II)	50	58	80	98	100	28
Mn(II)	50	67	150	440	$>10^3$	$>10^3$
Co(II)	62	84	200	10^3	$>10^3$	$>10^3$
Ni(II)	70	100	230	$>10^3$	$>10^3$	$>10^3$

TABLE III.—DISTRIBUTION COEFFICIENTS IN AQUEOUS n-PROPANOLIC 0·6*M* HYDROBROMIC ACID

Ion	n-Propanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	75	200	800	$>10^3$	$>10^3$	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	17	18	19	28	56
V(IV)	22	27	45	88	240	400
Fe(III)	430	$>10^3$	$>10^3$	$>10^3$	$>10^3$	120
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	15	14	10	4	<1
Bi(III)	3	3	3	2	1	<1
Mg(II)	36	40	68	180	800	$>10^3$
Ca(II)	90	150	320	$>10^3$	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	44	31	15	5	5
Zn(II)	55	76	124	108	11	1
Cd(II)	2	<1	<1	<1	<1	<1
Cu(II)	50	68	108	165	12	<1
Mn(II)	50	78	130	280	900	$>10^3$
Co(II)	62	75	130	260	$>10^3$	$>10^3$
Ni(II)	70	80	180	$>10^3$	$>10^3$	$>10^3$

TABLE IV.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ISOPROPANOLIC 0·6*M* HYDROBROMIC ACID

Ion	Isopropanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	75	200	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	10	12	13	17	27
V(IV)	22	28	50	120	500	10^3
Fe(III)	430	$>10^3$	$>10^3$	$>10^3$	$>10^3$	89
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	15	14	3	2	<1
Bi(III)	3	3	2	2	<1	<1
Mg(II)	36	48	64	260	$>10^3$	$>10^3$
Ca(II)	90	160	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	43	40	20	9	9
Zn(II)	55	74	142	100	1	<1
Cd(II)	2	<1	<1	<1	<1	<1
Cu(II)	50	58	120	85	3	<1
Mn(II)	50	72	170	430	$>10^3$	$>10^3$
Co(II)	62	78	170	600	$>10^3$	$>10^3$
Ni(II)	70	95	200	$>10^3$	$>10^3$	$>10^3$

hydrobromic acid–aliphatic alcohol systems are much less suitable than the corresponding hydrochloric acid systems.[2] With respect to separation of uranium from thorium and cerium they are also inferior to pure aqueous systems which are 0·6*M* or 0·9*M* (see Table XVII) or 8–12*M* in hydrobromic acid.[1]

Molybdenum(VI) and *vanadium(IV)*. While the adsorption of molybdenum does not show significant changes when the concentration of aliphatic alcohols increases from 0 to 90% (see Tables I–IV), the retention of vanadium(IV) increases regularly to reach its highest adsorption value in the presence of 90% aliphatic alcohol. However, the differences in the adsorption behaviour of these two elements do not suggest the possibility of clean-cut separations of molybdenum from vanadium. Similar unfavourable conditions exist in pure aqueous hydrobromic acid systems (see Table XVII).[1] A decrease of the hydrobromic acid concentration at a fixed 90% concentration of aliphatic alcohol (see Tables IX–XII) means an increase of vanadium adsorption which is also observed, though to a less extent, in pure aqueous hydrobromic acid systems[1] (see also Table XVII). On the other hand the retention of molybdenum increases only slightly except for the values of $>10^3$ in the media containing methanol or n-propanol. This high adsorption from these two systems may be due to partial reduction of molybdenum to a lower valency state which is more strongly retained by the resin than is molybdenum(VI).

Iron(III), aluminium(III), indium(III) and bismuth(III). In 0·6*M* hydrobromic acid media with varying concentrations of methanol and ethanol (see Tables I and II) the adsorption of iron increases with an increase of the concentration of these two organic solvents in the entire concentration range from 20 to 90%. Maximum adsorption is observed in media containing 20–80% n-propanol or isopropanol which is followed by minimum adsorption in the presence of 90% of the organic solvents (see Tables III and IV). In hydrochloric acid–aliphatic alcohol media of analogous composition the distribution coefficient of iron was found[2] to decrease to very low values with an increase in the concentration of all the aliphatic alcohols. An increase of the hydrobromic acid concentration (see Tables IX–XII) shows the expected decrease of iron adsorption in all aliphatic alcohols. This decrease is most pronounced in the n-propanol and isopropanol systems.

Like thorium and cerium, aluminium is in all cases strongly adsorbed (distribution coefficients $>10^3$) at all concentrations of aliphatic alcohols and hydrobromic acid. Thus, its behaviour is similar to that observed in aliphatic alcohol media containing hydrochloric acid.[2]

An increase in the concentration of aliphatic alcohols decreases the adsorption of both indium and bismuth to values which are <1 in the mixtures containing 80 or 90% alcohol. This means that ready separation of these two elements can be achieved not only from aluminium but also from uranium, thorium and cerium. Similar results were obtained in hydrochloric acid–aliphatic alcohol media of the same composition.[2] Separations of indium from bismuth in 0·6*M* hydrobromic acid–aliphatic alcohol systems are not readily achieved, because of the similarity and low values of their distribution coefficients. However, at a hydrobromic acid concentration of 0·15*M* (see Tables IX–XII) effective separations of these two elements should be possible. Here the separation factors ($K_{d\text{In}}/K_{d\text{Bi}}$) have values of >23–>57 which are greater by about one order of magnitude than those measured at other hydrobromic acid concentrations. Separations of indium from bismuth can also be achieved in pure aqueous systems containing low concentrations of hydrobromic acid (see Table XVII) or in media which are 8–12*M* in this acid.[1]

Magnesium(II), calcium(II), strontium(II) and *lead(II)*. When the alcohol concentration is increased the adsorption of magnesium, calcium and strontium increases regularly as the aliphatic alcohol concentration increases from 0 to 90%. The adsorption of magnesium is always lower than that of calcium, whilst strontium is invariably more strongly retained than is calcium or magnesium. As in the hydrochloric acid–aliphatic alcohol systems[2] a simple separation of these three elements is not possible, because of the similarity of the distribution coefficients. With an increase in acidity only the distribution coefficient of magnesium decreases while the coefficients of calcium and strontium remain $>10^3$ in the entire range of acidity from 0·15*M* to 0·9*M* hydrobromic acid (see Tables IX–XII).

In contrast to hydrochloric acid–aliphatic alcohol media in which the adsorption of lead increases with an increase in the concentration of alcohol,[2] the conditions are reversed in the hydrobromic acid systems. In the latter the adsorption of lead invariably decreases but not as rapidly as that of bismuth so that separation of lead from bismuth is possible with several systems. The separability is even greater when the acidity is decreased to 0·15*M* (see Tables IX–XII). From the tables it is also seen that the adsorption of lead shows the expected decrease with an increase of the hydrobromic acid concentration. It should be mentioned here that a separation of lead from bismuth is also possible in pure aqueous hydrobromic acid systems (see Table XVII) which are 0·15–0·6*M* in this acid but not in 0·9*M* or higher acid concentrations.[1]

Zinc(II) and cadmium(II). The adsorption of zinc from aliphatic alcohols increases when the concentration of the organic component in the mixtures is increased. Maximum adsorption is reached in 40% alcohol whereafter the distribution coefficient decreases to reach a value of 1 or <1 in 90% alcohol. On the other hand neither an increase nor a maximum is observed in the case of cadmium, which shows a distribution coefficient which invariably is <1 at all concentrations of aliphatic alcohols. A similar behaviour of cadmium is observed in 90% aliphatic alcohol media containing 10% of hydrobromic acid of varied molarity. In these media, however, zinc also shows a relatively high adsorption especially at low hydrobromic acid concentrations.

Very effective separations of zinc from cadmium can be achieved. In Table XVIII are shown the separation characteristics of three zinc–cadmium separations. Because of the very high separation factors (>110–300) these separations are much more effective than those in hydrochloric acid–aliphatic alcohol media[2] or those which could possibly be achieved in pure aqueous hydrobromic acid solutions (see Table XVII).

Copper(II) and manganese(II). The adsorption of copper increases with an increase of the concentration of aliphatic alcohols. Maximum adsorption values are obtained in 60–80% methanol, 80% ethanol, 60% n-propanol and 40% isopropanol. At higher alcohol concentrations its distribution coefficients drop rapidly and values as low as <1 have been measured in 90% n-propanol and isopropanol. A similar behaviour of copper, although much less pronounced, has been observed in hydrochloric acid–aliphatic alcohol media.[2]

Unlike copper, manganese does not show maximum adsorption values in any of the aliphatic alcohols but its adsorption increases rather regularly with an increase in the alcohol concentration, very high distribution coefficients being reached (mostly $>10^3$) at 90% alcohol concentration. Little variation of the manganese adsorption is observed when the concentration in hydrobromic acid is varied (see Tables IX–XII).

For very effective separations of copper from manganese, 90% n-propanol or isopropanol mixtures containing 10% of 3–9*M* hydrobromic acid can be used. In these cases the separation factors Mn/Cu are $>10^3$. No separation of copper from manganese is possible in pure aqueous hydrobromic acid media (see Table XVII).[1]

Cobalt(II) and nickel(II). In virtually all cases cobalt and nickel show the same adsorption pattern, *i.e.*, their distribution coefficients increase with increasing concentration of aliphatic alcohols. The adsorption of cobalt is invariably lower than that of nickel but the distribution coefficients are not sufficiently different for separation purposes. At high alcohol concentrations, however, both elements can be separated from molybdenum, indium, bismuth, lead, zinc, cadmium and copper. Similar separation possibilities exist with aliphatic alcohols containing varying concentrations of hydrobromic acid. Also in these systems the distribution coefficients of cobalt and nickel are of the same order of magnitude so that no separations of these elements from each other can be effected. The same observations have been made in pure aqueous hydrobromic acid media of low (see Table XVII) or high acidity.[1]

Methyl glycol media

The results of measurements of the distribution coefficients of the various elements in hydrobromic acid-methyl glycol media are shown in Tables V and XIII.

Uranium(VI), thorium(IV) and cerium(III). The behaviour of thorium and cerium in media containing varying concentrations of methyl glycol and hydrobromic acid is virtually the same as that observed in the hydrobromic acid–aliphatic alcohol mixtures. Uranium shows a somewhat different adsorption behaviour because its distribution coefficients in 90% methyl glycol, especially at hydrobromic acid concentrations of 0·6*M* or higher, are lower than those measured in the aliphatic alcohols. Nevertheless these adsorption values are still too high to allow rapid separations of uranium from thorium and/or cerium.

TABLE V.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROBROMIC ACID IN AQUEOUS METHYL GLYCOL SOLUTION

Ion	Methyl glycol concentration, %					
	0	20	40	60	80	90
UO_2(II)	75	100	150	700	$>10^3$	85
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	5	4	4	2	<1
V(IV)	22	19	21	24	43	93
Fe(III)	430	$>10^3$	$>10^3$	$>10^3$	220	<1
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	15	9	2	1	1
Bi(III)	3	<1	<1	1	4	4
Mg(II)	36	34	75	190	320	230
Ca(II)	90	150	330	$>10^3$	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	47	43	19	5	4
Zn(II)	55	91	92	26	<1	<1
Cd(II)	2	1	1	1	1	1
Cu(II)	50	68	96	2	1	<1
Mn(II)	50	62	110	290	10^3	440
Co(II)	62	71	120	360	700	270
Ni(II)	70	70	150	$>10^3$	$>10^3$	10^3

Molybdenum(VI) and vanadium(IV). These two elements show adsorption characteristics similar to those observed in aliphatic alcohol media. However, the distribution coefficient of molybdenum is considerably lower in methyl glycol so that separations of molybdenum from vanadium are possible at all hydrobromic acid concentrations (see Table XIII).

Iron(III), aluminium(III), indium(III) and bismuth(III). The adsorption of iron(III) decreases considerably at high methyl glycol and high hydrobromic acid concentrations whereby its distribution coefficients reach values which are <1, suggesting strong anionic complex formation under these conditions. That this is not the case, however, has been shown when Dowex 1 (in the bromide form) is used in place of Dowex 50. On this strongly basic anion-exchanger (Dowex 1) iron is also not retained. Consequently this behaviour of iron in methyl glycol and also in acetic acid, acetone and tetrahydrofuran media (see Tables VI–VIII and XIV–XVI) is due to an extraction effect which prevents the adsorption of iron on both exchangers. This effect, which is also observed with other elements and in several other mineral acid–organic solvent systems, has been demonstrated in previous publications.[2,3,5–10] Separations which are based on this principle have been termed CIESE (Combined Ion-Exchange–Solvent Extraction).[6,9,10]

In the case of hydrobromic acid–methyl glycol media this non-adsorbability of iron allows its separation from uranium, thorium, cerium, vanadium, aluminium, magnesium, calcium, strontium, manganese, cobalt and nickel.

Table VI.—Distribution coefficients in 0·6*M* hydrobromic acid in aqueous acetic acid

Ion	Acetic acid concentration, %					
	0	20	40	60	80	90
UO_2(II)	75	60	100	150	640	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	10	14	23	6	3
V(IV)	22	<1	<1	1	7	16
Fe(III)	430	$>10^3$	$>10^3$	$>10^3$	2	<1
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	10	7	4	2	2
Bi(III)	3	3	3	4	4	5
Mg(II)	36	47	75	110	490	165
Ca(II)	90	170	260	540	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	30	14	8	ppt	ppt
Zn(II)	55	80	40	2	1	1
Cd(II)	2	2	2	2	2	2
Cu(II)	50	70	90	34	1	<1
Mn(II)	50	75	110	165	210	60
Co(II)	62	68	130	140	110	17
Ni(II)	70	90	140	230	230	120

Table VII.—Distribution coefficients in 0·6*M* hydrobromic acid in aqueous tetrahydrofuran

Ion	Tetrahydrofuran concentration, %					
	0	20	40	60	80	90
UO_2(II)	75	90	150	410	160	110
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	8	5	<1	<1	<1
V(IV)	22	10	11	15	68	45
Fe(III)	430	$>10^3$	$>10^3$	$>10^3$	6	3
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	16	6	3	2	2
Bi(III)	3	<1	<1	3	3	4
Mg(II)	36	36	85	210	360	150
Ca(II)	90	125	240	$>10^3$	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	43	17	6	3	3
Zn(II)	55	56	56	9	3	3
Cd(II)	2	<1	<1	2	2	4
Cu(II)	50	64	87	38	1	<1
Mn(II)	50	56	140	$>10^3$	900	110
Co(II)	62	76	150	360	570	36
Ni(II)	70	90	210	$>10^3$	$>10^3$	90

Aluminium is strongly adsorbed at all concentrations of methyl glycol and hydrobromic acid, and indium and bismuth also show behaviour similar to that observed in the aliphatic alcohols.

Magnesium(II), calcium(II), strontium(II) and lead(II). These elements show in hydrobromic acid–methyl glycol media a behaviour which is similar to that observed

Table VIII.—Distribution coefficients in 0·6*M* hydrobromic acid in aqueous acetone

Ion	Acetone concentration, %					
	0	20	40	60	80	90
UO_2(II)	75	300	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	10	14	30	31	<1
V(IV)	22	32	54	105	250	146
Fe(III)	430	$>10^3$	$>10^3$	$>10^3$	2	<1
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	15	14	10	2	1	<1
Bi(III)	3	3	3	2	2	2
Mg(II)	36	45	100	260	$>10^3$	400
Ca(II)	90	155	570	$>10^3$	$>10^3$	$>10^3$
Sr(II)	700	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	48	43	26	6	4	3
Zn(II)	55	90	91	9	<1	<1
Cd(II)	2	1	1	1	<1	<1
Cu(II)	50	71	155	84	<1	<1
Mn(II)	50	67	130	600	900	82
Co(II)	62	75	150	$>10^3$	$>10^3$	9
Ni(II)	70	95	270	$>10^3$	$>10^3$	340

Table IX.—Distribution coefficients in 90% methanol mixtures containing 10% of hydrobromic acid of varied molarity

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	$>10^3$	$>10^3$	600	100
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	$>10^3$	29	23	14
V(IV)	240	220	106	42
Fe(III)	$>10^3$	$>10^3$	$>10^3$	63
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	23	2	<1	<1
Bi(III)	<1	<1	<1	<1
Mg(II)	$>10^3$	600	170	58
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	88	6	1	<1
Zn(II)	160	12	<1	<1
Cd(II)	<1	<1	<1	<1
Cu(II)	$>10^3$	270	30	5
Mn(II)	$>10^3$	$>10^3$	500	110
Co(II)	$>10^3$	$>10^3$	290	88
Ni(II)	$>10^3$	$>10^3$	300	100

Table X.—Distribution coefficients in 90% ethanol mixtures containing 10% of hydrobromic acid of varied molarity

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO$_2$(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	32	20	16	10
V(IV)	$>10^3$	$>10^3$	380	140
Fe(III)	$>10^3$	$>10^3$	$>10^3$	75
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	52	6	<1	<1
Bi(III)	1	1	<1	<1
Mg(II)	$>10^3$	$>10^3$	$>10^3$	340
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	35	2	2	<1
Zn(II)	300	20	<1	<1
Cd(II)	1	<1	<1	<1
Cu(II)	380	240	28	6
Mn(II)	$>10^3$	$>10^3$	$>10^3$	900
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$

Table XI.—Distribution coefficients in 90% n-propanol mixtures containing 10% of hydrobromic acid of varied molarity

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO$_2$(II)	$>10^3$	$>10^3$	$>10^3$	400
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	$>10^3$	70	56	52
V(IV)	$>10^3$	10^3	400	180
Fe(III)	$>10^3$	$>10^3$	120	10
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	57	3	<1	<1
Bi(III)	<1	<1	<1	<1
Mg(II)	$>10^3$	$>10^3$	$>10^3$	600
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	58	14	5	<1
Zn(II)	400	148	1	<1
Cd(II)	<1	<1	<1	<1
Cu(II)	5	<1	<1	<1
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	$>10^3$	$>10^3$	$>10^3$	400
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$

in the aliphatic alcohols. However, separation possibilities for lead from bismuth exist only in 0·6*M* hydrobromic acid media containing 0–60% methyl glycol.

Zinc(II) and cadmium(II). Both elements show the same very low adsorption at all hydrobromic acid concentrations (see Table XIII) so that separations are only possible under the conditions mentioned above for lead and bismuth.

TABLE XII.—DISTRIBUTION COEFFICIENTS IN 90% ISOPROPANOL MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	17	21	27	110
V(IV)	$>10^3$	$>10^3$	10^3	530
Fe(III)	$>10^3$	$>10^3$	89	3
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	26	1	<1	<1
Bi(III)	<1	<1	<1	<1
Mg(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	130	19	9	1
Zn(II)	120	9	<1	<1
Cd(II)	<1	<1	<1	<1
Cu(II)	2	<1	<1	<1
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$

Copper(II), manganese(II), cobalt(II) and nickel(II). These elements show in hydrobromic acid–methyl glycol media a behaviour which is similar to that observed in aliphatic alcohols. Separations of copper from manganese and also nickel and cobalt can be effected at all hydrobromic acid concentrations (see Table XIII) and also in 0·6*M* hydrobromic acid media which contain 60–80% methyl glycol (see Table V).

Acetone and tetrahydrofuran media

In Tables VII, VIII, XV and XVI are shown the results of determinations of the distribution coefficients of the various metal ions in acetone and tetrahydrofuran media containing hydrobromic acid. The elements show a similar behaviour in both organic solvents, except in the case of uranium which is considerably less strongly retained from tetrahydrofuran media than from the corresponding hydrobromic acid–acetone systems.

Thorium, cerium, aluminium, indium, bismuth, magnesium, calcium, strontium, lead, zinc, cadmium, copper, manganese, cobalt and nickel show a behaviour similar to that observed in aliphatic alcohol media.

As in the methyl glycol systems the difference between the distribution coefficients of molybdenum and vanadium in acetone media are sufficiently high to allow successful separations of these elements. The characteristics of two of such separations are outlined in Table XVIII. Similarly, the extraction effect mentioned above (under *Methyl glycol media*) can be used to separate iron from uranium in both acetone and tetrahydrofuran media containing hydrobromic acid. Results for two iron–uranium separations are recorded in Table XVIII.

Table XIII.—Distribution coefficients in 90% methyl glycol mixtures containing 10% of hydrobromic acid of varied molarity

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	600	220	85	52
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	<1	<1	<1	<1
V(IV)	130	110	93	48
Fe(III)	$>10^3$	52	<1	<1
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	1	1	1	21
Bi(III)	2	3	4	5
Mg(II)	$>10^3$	$>10^3$	230	88
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	7	6	4	3
Zn(II)	1	<1	<1	<1
Cd(II)	2	<1	1	2
Cu(II)	2	<1	<1	<1
Mn(II)	$>10^3$	$>10^3$	440	92
Co(II)	$>10^3$	$>10^3$	270	60
Ni(II)	$>10^3$	$>10^3$	10^3	100

Table XIV.—Distribution coefficients in 90% acetic acid mixtures containing 10% of hydrobromic acid of varied molarity

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	270	420	$>10^3$	270
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	1	3	3	3
V(IV)	21	25	16	14
Fe(III)	<1	<1	<1	<1
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	<1	<1	2	3
Bi(III)	<1	4	5	6
Mg(II)	$>10^3$	10^3	165	100
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	ppt	ppt	ppt	ppt
Zn(II)	1	1	1	1
Cd(II)	2	3	2	4
Cu(II)	1	<1	<1	<1
Mn(II)	$>10^3$	590	60	24
Co(II)	$>10^3$	250	17	4
Ni(II)	$>10^3$	$>10^3$	120	35

TABLE XV.—DISTRIBUTION COEFFICIENTS IN 90% TETRAHYDROFURAN MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	$>10^3$	$>10^3$	110	42
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	<1	<1	<1	<1
V(IV)	300	265	45	24
Fe(III)	$>10^3$	3	3	3
Al(III)	560	216	$>10^3$	700
In(III)	<1	2	2	2
Bi(III)	2	2	4	2
Mg(II)	$>10^3$	600	150	60
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	5	4	3	2
Zn(II)	5	6	3	6
Cd(II)	2	2	4	4
Cu(II)	4	1	<1	<1
Mn(II)	$>10^3$	$>10^3$	110	21
Co(II)	$>10^3$	560	36	7
Ni(II)	$>10^3$	$>10^3$	90	28

TABLE XVI.—DISTRIBUTION COEFFICIENTS IN 90% ACETONE MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	100	32	<1	<1
V(IV)	$>10^3$	800	146	73
Fe(III)	4	<1	<1	<1
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	<1	<1	<1	<1
Bi(III)	<1	<1	2	3
Mg(II)	$>10^3$	$>10^3$	400	130
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	1	2	3	4
Zn(II)	<1	<1	<1	<1
Cd(II)	<1	<1	<1	<1
Cu(II)	<1	<1	<1	<1
Mn(II)	$>10^3$	$>10^3$	82	4
Co(II)	$>10^3$	750	9	1
Ni(II)	$>10^3$	10^3	340	80

TABLE XVII.—DISTRIBUTION COEFFICIENTS IN HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	$>10^3$	800	75	30
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	32	18	7	11
V(IV)	120	74	22	11
Fe(III)	$>10^3$	$>10^3$	430	137
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	$>10^3$	600	15	11
Bi(III)	15	2	3	4
Mg(II)	$>10^3$	110	36	18
Ca(II)	$>10^3$	350	90	40
Sr(II)	$>10^3$	$>10^3$	700	145
Pb(II)	$>10^3$	275	48	8
Zn(II)	$>10^3$	300	55	23
Cd(II)	120	12	2	1
Cu(II)	ppt	290	50	30
Mn(II)	$>10^3$	180	50	22
Co(II)	$>10^3$	280	62	27
Ni(II)	$>10^3$	400	70	30

TABLE XVIII—EXAMPLES OF SEPARATIONS IN HYDROBROMIC ACID–ORGANIC SOLVENT MEDIA (ON A 1g COLUMN; DIAMETER = 0·5 cm.)

Metal Ions separated (2·5 mg of each)	Composition of eluent	Breakthrough volume, *ml*	Elution volume, *ml*	Distribution coefficient
Zn(II)—Cd(II)	90% ethanol– 0·15*M* HBr	Cd 1·0 Zn 160	Cd 5·0	Cd 1 Zn 300
Zn(II)—Cd(II)	40% ethanol– 0·6*M* HBr	Cd 0·5 Zn 65	Cd 3·0	Cd <1 Zn 110
Zn(II)—Cd(II)	90% methanol– 0·15*M* HBr	Cd 0·5 Zn 100	Cd 5·5	Cd <1 Zn 160
Mo(VI)—V(IV)	90% acetone– 0·6*M* HBr	Mo $<1·0$ V $\gg 16$	Mo 16	Mo <1 V 146
Mo(VI)—V(IV)	90% acetone– 0·9*M* HBr	Mo $<1·0$ V 22·5	Mo 41	Mo <1 V 73
U(VI)—Fe(III)	90% acetone– 0·9*M* HBr	Fe 3·0 U $\gg 13$	Fe 13	Fe <1 U $>10^3$
U(VI)—Fe(III)	90% tetra-hydrofuran– 0·3*M* HBr	Fe $<1·0$ U $\gg 15$	Fe 15	Fe 3 U $>10^3$

Acetic acid media

The results of measurements of distribution coefficients of the elements in acetic acid media containing hydrobromic acid are shown in Tables VI and XIV. A comparison of these with those representing the systems discussed before shows that the behaviour of the elements in acetic acid is very similar to that in the other organic solvents.

Water media

In Table XVII the behaviour of the elements in pure aqueous solutions containing varying concentrations of hydrobromic acid is shown. In these systems fewer possibilities exist for the separation of the various metal ions from one another than in the media containing organic solvents. This is demonstrated by the separation examples listed in Table XVIII.

Zusammenfassung—Das Kationenaustauschverhalten von 19 Elementen in Medien aus Bromwasserstoffsäure und organischen Lösungsmitteln wurde untersucht. In diesen Systemen wurden die Verteilungskoeffizienten der Metallionen an dem stark sauren Kationenaustauschharz Dowex 50; X8 ermittelt. Als organische Lösungsmittel wurden Methanol, Äthanol, n-Propanol, Isopropanol, Methylglycol, Aceton, Tetrahydrofuran und Essigsäure verwendet. Die zur quantitativen Trennung der Elemente am besten geeigneten Bedingungen werden mitgeteilt und diskutiert. Mehrere Beispiele erfolgreicher Trennungen sind in einer Tabelle angegeben.

Résumé—On a étudié les caractéristiques d'échange de cations de 19 éléments en milieux acide bromhydrique-solvant organique. Dans ces systèmes, on a déterminé les séries de coefficients de partage des ions métalliques en utilisant la résine échangeuse de cations fortement acide Dowex 50, X8. Comme solvants organiques, on a employé les méthanol, éthanol, *n*-propanol, isopropanol, méthylglycol, acétone, tétrahydrofuran et acide acétique. On indique les conditions les plus convenables pour la séparation quantitative des éléments et en discute. On indique sous forme de table plusieurs exemples de séparations couronnées de succès.

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PHENYL 2-(6-METHYLPYRIDYL) KETONE OXIME

A REAGENT FOR COPPER IN ALKALIS

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Summary—Phenyl 2-(6-methylpyridyl) ketone oxime (**R**) can be used for the determination of copper in alkalis, the orange CuR_2 being extracted into isoamyl alcohol and its absorbance measured. Owing to the stereochemical blocking action of the 6-methyl group, iron does not interfere. In acid solution an orange-yellow compound CuR_3 is formed, also extractable into isoamyl alcohol.

PHENYL 2-PYRIDYL KETONE OXIME was proposed as a spectrophotometric reagent for iron by Trusell and Diehl[1] in 1959. Although this reagent is not the most sensitive known for iron, the molar absorptivity of the iron(II) complex being $15{\cdot}6 \times 10^3$ (1,10-phenanthroline $11{\cdot}1 \times 10^3$; bathophenanthroline $22{\cdot}4 \times 10^3$), it is unique in that the iron(II) derivative is formed in highly alkaline solutions and can be extracted from such solutions into amyl alcohol; these characteristics provide not only a method for the direct determination of iron in alkalis but furnish a way of differentiating iron oxides from metallic iron.[1] A fair number of analytical applications have been developed since the reagent was first proposed,[2] a recent application, for example, being to the determination of the iron in ethylamines,[3] but perhaps the greatest use so far has been in the preparation of iron-free solutions of alkalis for enzyme studies.

One of the remarkable features of ferroin chemistry is the specificity for copper(I) conferred by substituents *ortho* to the nitrogen atoms of the 1,10-phenanthrolines and 2,2′-bipyridyls; this has made possible the extraordinary specificity and sensitivity and the numerous useful applications of the reagents cuproine (2,2′-biquinolyl), neocuproine (2,9-dimethyl-1,10-phenanthroline), and bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline).[4] In these reagents the adjacent substituents, the fused rings in cuproine and the methyl groups in the other two, exert a stereochemical effect which prevents three such molecules from entering the octahedral co-ordination sphere of atoms such as iron. No such effect, however, occurs in the tetrahedral co-ordination sphere of copper(I), the two molecules of reagent entering with ease to occupy planar positions at right angles to each other.

The present work is an extension of this blocking action to phenyl 2-pyridyl ketone oxime, the objective being to obtain a reagent which will at once be specific for copper, react in strongly alkaline solution, and form a copper compound which can be extracted into immiscible solvents. Phenyl 2-(6-methylpyridyl) ketone oxime proved easy to prepare and to have just the properties desired.

EXPERIMENTAL

Phenyl 2-(6-methylpyridyl) ketone oxime

To 5 g of 2-benzoyl-6-methylpyridine dissolved in 20 ml of 95% ethanol were added 3·75 g of hydroxylammonium chloride dissolved in 5 ml of water, and 2·5 g of sodium hydroxide dissolved in 5 ml of water. The mixture was heated to 85–90° for 1 hr and then allowed to cool to room temperature. Solid carbon dioxide was added to the mixture in sufficient amount to bring the pH to about 7, causing the oxime to precipitate. The precipitate was filtered off, thoroughly washed with water and dried at 60° under reduced pressure; m.p. 103–135°. This material was refluxed for 15 min in the minimum amount of chloroform required to dissolve all of the solid. On cooling, crystals separated which were filtered off, recrystallized three times from hot ethanol and then dried at 60° under reduced pressure; white crystals, m.p. 133–134°; found; C 73·3%, H 5·5%, N 13·0%; calculated for $C_{13}H_{12}N_2O$; C 73·57%, H 5·7%, N 13·20%.

Reagents

Phenyl 2-(6-methylpyridyl) ketone oxime solution, "reagent solution", 0·1% in ethanol.

Standard copper(II) sulphate, $5 \times 10^{-4}M$: Prepared from anhydrous copper sulphate dissolved in dilute sulphuric acid and diluted with water, or from metallic copper dissolved in nitric and sulphuric acids and diluted with water.

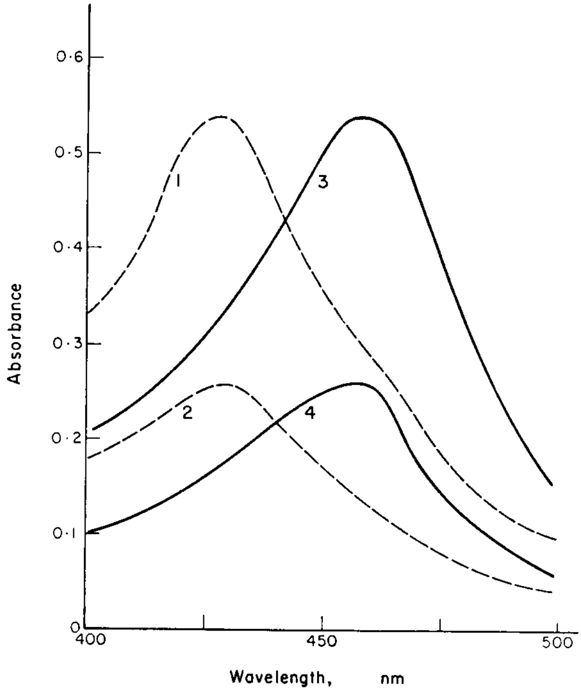


FIG. 1.—Absorption spectra of the copper(I) derivatives of phenyl 2-(6-methylpyridyl) ketone oxime (R) in aqueous solution.

1—CuR_3, [Cu] = $5{\cdot}0 \times 10^{-5}M$, pH 4·5
2—CuR_3, [Cu] = $2{\cdot}5 \times 10^{-5}M$, pH 4·5
3—CuR_2, [Cu] = $5{\cdot}0 \times 10^{-5}M$, pH 12·0
4—CuR_2, [Cu] = $2{\cdot}5 \times 10^{-5}M$, pH 12·0

Hydroxylammonium chloride, 10% solution, copper-free. To a solution of 100 g of hydroxylammonium chloride in 1 l. of water add 5 ml of 0·1% reagent solution, adjust the pH to 7 with sodium hydroxide, and extract with 10 ml of isoamyl alcohol.

Sodium hydroxide, 10M, copper-free. Treat a solution of 400 g of sodium hydroxide in 1 l. of water with 5 ml of 0·1% reagent solution and 5 ml of 10% hydroxylammonium chloride solution and extract with 10 ml of isoamyl alcohol.

Absorption spectra and effect of pH

Solutions of copper, 0, $2{\cdot}5 \times 10^{-5}$, and $5{\cdot}0 \times 10^{-5}M$ respectively, containing an excess of hydroxylammonium chloride and reagent, were adjusted to pH 4·5 or 12·0 and their absorption spectra recorded (Fig. 1).

A series of solutions was prepared, the final concentration of copper in each being $5{\cdot}0 \times 10^{-5}M$ and each containing 5 ml of 0·1% reagent solution and 2 ml of 10% hydroxylammonium chloride

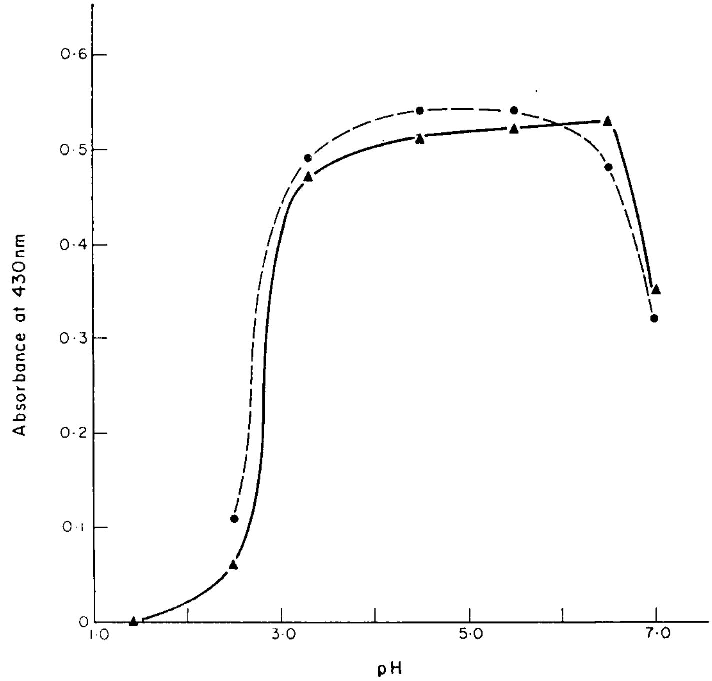


Fig. 2.—Effect of pH on the formation of the orange-yellow compound CuR_3. ▲—In aqueous phase; ●—in isoamyl alcohol phase.

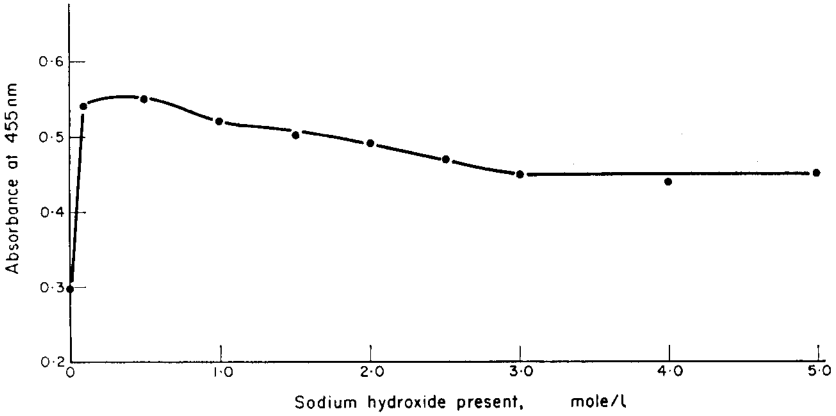


Fig. 3.—Effect of concentration of alkali on the formation of the orange compound CuR_2.
Copper(I) = $5{\cdot}0 \times 10^{-5}M$.

solution in the final volume of 50·00 ml. The pH was adjusted with dilute sulphuric acid or sodium hydroxide to vary over the range 1·4–7. The absorbance was measured at 430 nm (Fig. 2).

A similar series was prepared and the amount of free sodium hydroxide varied from 0·1 to 5*M*. The absorbance was measured at 455 nm (Fig. 3).

Nature of the copper(I) compounds of phenyl 2-(6-methylpyridyl) ketone oxime

The mole-ratio method showed that a 1:2 copper:reagent complex was formed at pH 12·0 and a 1:3 complex at pH 4·3.

At pH 7–11 copper(I) and the reagent form a dark red insoluble material. Several grams of this material were prepared, filtered off, washed well with water and dried in a vacuum at 60°. A sample was dissolved in water by adjusting the pH to 12·0 with sodium hydroxide, and the absorbance measured at 430 and 455 nm. Two aliquots of this solution were then treated, one with additional copper and the other with reagent and the absorbances were measured. The dark red compound proved to be the 1:3 compound, see *Discussion*. Samples of the compound were titrated potentiometrically in non-aqueous media with acid and base.

Determination of copper in alkalis

To 25 g of sodium hydroxide in 100 ml of water in a separatory funnel add 5 ml of 10% hydroxylammonium chloride solution and 5 ml of 0·1% of reagent solution. Mix, add 5 ml of isoamyl alcohol and shake vigorously for 2 min. Let the phases separate, withdraw the lower layer, transfer the isoamyl alcohol layer to a 10·0-ml volumetric flask and dilute to volume with ethanol. Measure the absorbance of this solution at 455 nm. Prepare a calibration curve in a similar manner by adding various amounts of copper to 5*M* sodium hydroxide.

Typical results for copper in sodium hydroxide, potassium hydroxide, tris(hydroxymethyl)aminomethane and ammonia are given in Table I.

TABLE I.—DETERMINATION OF COPPER IN ALKALIS WITH PHENYL 2-(6-METHYLPYRIDYL) KETONE OXIME

Material	Copper added, *μg/g*	Copper found, *μg/g*	Recovery, %
Sodium hydroxide,		0·4	
analytical grade	12·5	12·5	97
Potassium hydroxide,		0·3	
analytical grade	12·5	13·0	101
Tris(hydroxymethyl)-aminomethane,		0·1	
analytical grade	12·5	0·1	0
Ammonia solution,		0·1	
analytical grade	12·5	4·0	32
Sodium hydroxide,		0·6	
U.S.P. grade	12·5	12·5	96

RESULTS AND DISCUSSION

Preparation, structure and properties of phenyl 2-(6-*methylpyridyl*) *ketone oxime*

The method of oximating 2-benzoyl-6-methylpyridine was that used for 2-benzoylpyridine by Huntress and Walker[5] as modified by Trusell and Diehl.[1] As with phenyl 2-pyridyl ketone oxime, a mixture of the two possible isomers is obtained and can be separated by recrystallization first from chloroform and then repeatedly from ethanol. The isomer isolated, m.p. 133–134°, reacted with copper(I) and is presumed to be the *syn*-form. The *anti*-form undergoes slow conversion into the *syn*-form, a phenomenon observed with phenyl 2-pyridyl ketone oxime and studied in detail by Vassian and Murmann.[6]

Two copper(I) compounds of phenyl 2-(6-methylpyridyl) ketone oxime are formed, an orange-yellow compound in acid solution, and an orange compound in alkaline solution; an insoluble dark red compound forms in slightly alkaline solution, pH 7–11·5, but dissolves on the addition of either acid or alkali. Both the yellow and the orange compounds (and the insoluble material) pass readily and quantitatively from the aqueous phase into isoamyl alcohol.

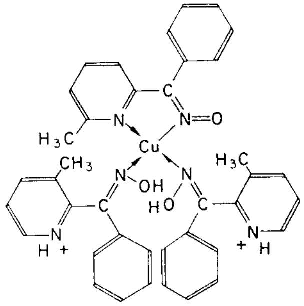
Copper(I) is converted quantitatively into the 1:3 compound in the presence of excess of reagent over the pH range 3·5–6·5, Fig. 2. The wavelength of maximum absorbance (Fig. 1) is 425–430 nm, the molar absorptivity being $10·8 \times 10^3$.

Copper(I) is converted quantitatively into the 1:2 compound in the presence of excess of reagent at pH values >12 and in solutions at least 5*M* in alkali, Fig. 3. The wavelength of maximum absorption is 455–460 nm, the molar absorptivity being $11{\cdot}0 \times 10^3$ in 0·25–0·5*M* sodium hydroxide.

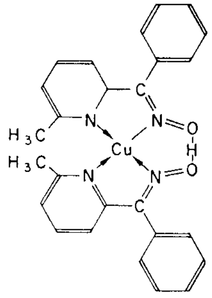
The dark red compound precipitated at pH 7–11·5 proved to be the 1:3 compound. When the solid was dissolved in alkali, reagent was liberated, as was demonstrated by the increase in colour on addition of copper. When the solid was dissolved in acid, however, no increase in colour was obtained on addition of either copper or reagent.

Non-aqueous potentiometric titration of the dark red compound with acetic acid gave a curve with a well-defined point of inflection. Moreover, just twice as much acid was consumed when a sample weighing twice as much was titrated. Two moles of acid were used for each one of copper present and this is interpreted as implying the presence of two free pyridyl groups, that is, not bound to copper and free for titration. On electrophoresis at pH 8·6 in a 0·05*M* veronal buffer, the 1:3 compound did not move, indicating that it carries zero charge.

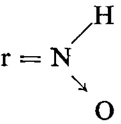
For the two copper(I) compounds of phenyl 2-(6-methylpyridyl) ketone oxime we propose structures **I** and **II**.



I—Orange-yellow, 1:3 copper:reagent compound present in acid solution



II—Orange 1:2 copper:reagent compound present in alkaline solution

These formulations are based on the known behaviour of the oxime group: it enters the co-ordination sphere of a metal ion both as an acidic group and as a simple co-ordinating group, and as an acid it functions as the nitrone tautomer  $= N\begin{array}{l}\nearrow H\\ \searrow O\end{array}$ (for a review of this argument see the monograph by Diehl[7]). The *syn*-isomer is the reactive isomer. Hydrogen-bonding between two oxime groups is postulated in **II** but no evidence is offered as to its existence.

Phenyl 2-(6-methylpyridyl) ketone oxime is quite specific for copper. It gives no colour with bismuth, mercury, zinc, molybdenum, lead, tungsten, palladium and platinum. With it copper can be determined in the presence of 100 times as much iron if the compound is extracted into isoamyl alcohol. Cobalt appears to be the only element which interferes seriously. Copper may be determined in the presence of 100 times as much cobalt if the solution is made alkaline before the addition of reagent. If the reagent is added to the neutral solution, a coloured cobalt compound is formed. The molar absorptivity of this cobalt compound at pH 7·5 is 12·5 × 10^3 at 350 nm, the wavelength of maximum absorption; both extractability and colour formation appear to reach a maximum at about pH 7.

Our original hope of obtaining a reagent for determining copper in alkalis was fulfilled, for recoveries of copper added to sodium hydroxide were quantitative, Table I. Recovery was only partial from ammonia and no copper was recovered at all from tris(hydroxymethyl)aminomethane. The latter fact was surprising as tris(hydroxylmethyl)aminomethane has not normally been considered to form non-dissociated compounds with copper.

Although the reagent was developed primarily for the determination of copper in strongly alkaline solutions, it is apparent that it should be useful for the preparation of copper-free alkalis.

Zusammenfassung—Phenyl-2-(6-methylpyridyl)ketonoxim (**R**) kann zur Bestimmung von Kupfer in Alkalien verwendet werden; das orange CuR_2 wird in Isoamylalkohol extrahiert und seine Extinktion gemessen. Wegen der stereochemischen Blockierung durch die Methylgruppe in 6-Stellung stört Eisen nicht. In saurer Lösung bildet sich eine orange-gelbe Verbindung CuR_3, die sich auch in Isoamylalkohol extrahieren läßt.

Résumé—On peut utiliser l'oxime de la phényl 2-(6-méthylpyridyl) cétone (**R**) pour le dosage du cuivre dans les alcalis, le CuR_2 orangé étant extrait en alcool isoamylique et son absorption mesurée. A cause de l'action de blocage stéréochimique du groupement 6-méthyl, le fer ne gêne pas. En solution acide il se forme un composé orangé-jaune CuR_3, également extractible en alcool isoamylique.

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1,5-BIS(DICARBOXYMETHYLAMINOMETHYL)-2,6-DIHYDROXYNAPHTHALENE AS A SELECTIVE SPECTROFLUORIMETRIC REAGENT FOR CALCIUM

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Summary—1,5-Bis(dicarboxymethylaminomethyl)-2,6-dihydroxynaphthalene (BDDN) forms fluorescent complexes with aluminium, barium, beryllium, calcium, magnesium and strontium. All the complexes have 2:1 metal:ligand ratios. Barium, calcium, magnesium and strontium exhibit maximal fluorescence at pH 11·7, with excitation and emission maxima at 385 and 445 nm respectively. Aluminium and beryllium show maximal fluorescence at pH 5·8 and 5·2 respectively, the excitation and emission maxima being at 370 and 405 nm. The formation of the calcium complex provides a highly sensitive and selective determination of calcium in the range 10–500 ng. The fluorescence measurement of calcium should be made within 5 min of mixing the solutions because of the instability of the reagent at the given pH. Potassium cyanide may be used as a masking agent and ter- or quadrivalent cations should be removed by preliminary extraction with 8-hydroxyquinoline in chloroform at pH 6·0. In such conditions, of 33 cations studied, only magnesium (>20 ng), strontium (>70 ng) and barium (>150 ng) caused interference in the determination of 300 ng of calcium. Among 16 anions examined, only EDTA interfered seriously.

THE introduction of dicarboxymethylaminomethyl groups into reagents which exhibit fluorescence changes on deprotonation has been shown to product metallofluorescent molecules which act as highly sensitive reagents for the spectrofluorimetric determination of trace metals.[1–3] In a previous communication[3] we have shown how the introduction of this group into 3-hydroxy-2-naphthoic acid produces a reagent which is 10 times more sensitive for aluminium than the parent substance and which shows a highly selective action for scandium and lutetium. The present paper describes the introduction of two such groups into the molecule of 2,6-dihydroxynaphthalene to produce 1,5-bis(dicarboxymethylaminomethyl)-2,6-dihydroxynaphthalene (BDDN). The parent molecule exhibits a strong blue fluorescence in aqueous solution at pH > 8 and its derivative, BDDN, exhibits similar properties and strong selective metallofluorescence for a number of metal ions.

EXPERIMENTAL

Apparatus

Fluorescence measurements were made with a Farrand double monochromating spectrofluorimeter fitted with a 150-W Xenon arc lamp and RCA IP 28 photomultiplier. Fused quartz cells (10 × 20 × 50 mm) were used throughout. To obtain the maximum sensitivity compatible with good definition of maxima, 10-nm band-width slits were used in the exciting and analysing monochromators. Fluorescence was measured at right angles to the incident light, the mean solution path-length of exciting radiation being 5 mm and of fluorescent emission 10 mm.

Preparation of the reagent

Iminodiacetic acid, disodium salt (3·90 g, 0·02 mole) was dissolved in glacial acetic acid (50 ml) by warming to 50–60°; 2 ml of 38% aqueous formaldehyde were added, the flask was stoppered, shaken for 5 min, then 2,6-dihydroxynaphthalene (1·60 g, 0·01 mole) was added. Although the dihydroxynaphthalene dissolved very quickly, the shaking was continued for 5–10 min, whereupon a white crystalline product was precipitated. The mixture was heated to 60–70° and kept at that temperature for 5 hr; it was then cooled to room temperature and the precipitate collected by suction on a porosity 4 sintered-glass crucible and washed with absolute ethanol (200 ml). The precipitate was dried for 3 hr at 100° (yield of crude product, 4·10 g) and then suspended in boiling 20% aqueous sodium acetate solution (50 ml). The hot suspension was filtered by suction and the filtrate allowed to stand at room temperature for 3 days. The white crystalline product was filtered off by suction, washed with absolute ethanol (20 ml), recrystallized from 25 ml of hot water, by standing at room temperature for 3 days, collected on a porosity 3 or 4 glass filter, washed with absolute ethanol (10 ml), and dried in a desiccator over anhydrous calcium chloride at room temperature for 3 days. The yield was 0·80 g. Found: C 48·3%, H 4·3%, N 5·4%; $C_{20}H_{20}N_2O_{10}Na_2$ (m.w. 494·4) requires C 48·59%, H 4·08%, N 5·67%.

Reagents

Solutions, 1·00 × $10^{-4}M$, of BDDN and analytical grade metal salts; the solution of BDDN is stable for only 5 hr. Potassium cyanide, 0·01*M*; 8-Hydroxyquinoline, 0·1*M*, in chloroform. The acidity of solutions was adjusted with the following solutions: 9·35*M* perchloric acid (H° 5·00–0·50); 0·50*M* perchloric acid + 1·00*M* hexamine + 0·50*M* sodium perchlorate (pH 1·10–7·44); 1·00*M* hexamine + 0·50*M* sodium perchlorate + 0·50*M* sodium hydroxide (pH 7·44–13·00); 10·00*M* sodium hydroxide (pH 13·00–15·80). The ionic strength was kept constant (0·10*N*) in the pH range 1·10–13·00 throughout these experiments.

Determination of calcium with BDDN

When ter- and quadrivalent ions are present. Adjust a sample solution containing 10–500 ng of calcium to pH 6 (pH meter). Shake for 2 min each time with three 10-ml portions of 0·1*M* 8-hydroxyquinoline in chloroform. Remove traces of 8-hydroxyquinoline from the aqueous phase by shaking with two 20-ml portions of chloroform. Add 5·0 ml of 0·01*M* potassium cyanide and 0·50 ml of 0·50*M* sodium hydroxide and mix. Add 5·00 ml of 5·00 × $10^{-6}M$ BDDN, dilute to 25 ml with water and mix. After exactly 5 min, measure the fluorescence at 445 nm with the excitation monochromator set at 385 nm. Construct a calibration curve for 10–500 ng of calcium in the same way; a straight line should be obtained.

When ter- and quadrivalent ions are absent. Use the same procedure but without the 8-hydroxyquinoline extraction.

RESULTS AND DISCUSSION

Sensitivity

To counteract variations in the intensity of the xenon arc source and the response of the detector–amplifier system, all fluorescence intensities were expressed as the ratio of fluorescence of a freshly prepared standard quinine sulphate solution (8 × 10^{-4} g of quinine per litre of 10^{-3} *M* sulphuric acid) measured in the same cell at 450 nm with the excitation monochromator set at 350 nm. The relative molar fluorescence was expressed as the ratio of the calculated fluorescence of 1*M* metal sample solution to that of 1*M* quinine in $10^{-3}M$ sulphuric acid see Table IV.

BDDN was found to be ten times more sensitive than Calcein Blue[2] for the direct spectrofluorimetric determination of calcium. Also, the stability of BDDN in alkaline solution is better than Calcein Blue, which decomposes immediately an alkali is added.

Spectral characteristics

The spectral characteristics of the lamp and photomultiplier used have been given in previous papers from this laboratory.[4,5] The excitation and emission spectra of the calcium, strontium, barium and magnesium complexes are plotted in Fig. 1.

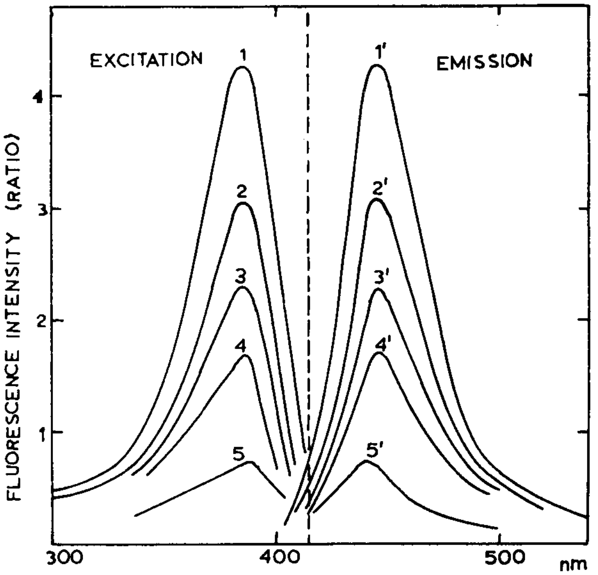


Fig. 1.—Excitation and emission spectra of calcium (1,1′), strontium (2,2′), magnesium (3,3′) and barium (4,4′) complexes with BDDN, and of BDDN alone (5,5′). $C_M = 2C_L = 4{\cdot}00 \times 10^{-6}M$, pH 11·70.

They are uncorrected for the variations in spectral response of the source and detector system. It will be seen that the fluorescence characteristics are essentially those of the reagent. The order of sensitivity is Ca > Sr > Mg > Ba.

The effect of pH on the fluorescence intensity of the reagent and its calcium, strontium, barium and magnesium complexes is given in Fig. 2. The maximum

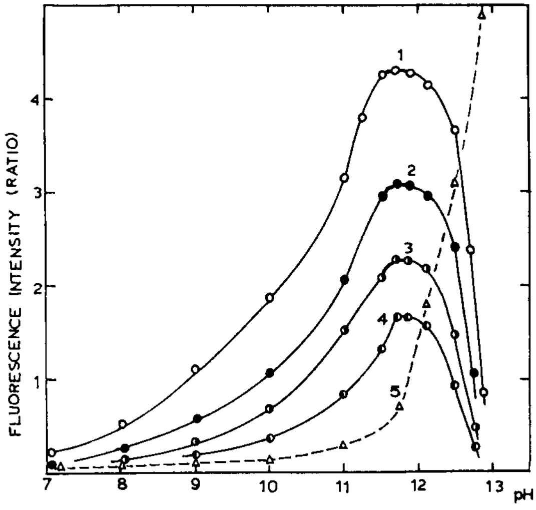


Fig. 2.—pH-Dependence of fluorescence of calcium (1), strontium (2), magnesium (3) and barium (4) complexes; (5) reagent alone.
$C_M = 2C_L = 4{\cdot}00 \times 10^{-6}M$, excitation 385 nm, emission 445 nm.

fluorescence of the complexes occurs at pH 11·8 with the excitation and emission maxima at 385 and 445 nm respectively. The fluorescence of the reagent is negligible at pH 7·0 and only very slight over the pH range 7–10. A small fluorescence occurs at pH 11·8, *cf.* Fig. 1, and must be deducted from the observed fluorescence for metal complexes. The excitation and emission maxima for the reagent are at 390 and 440 nm respectively but the fluorescence is much weaker than that of the metal complexes. The fluorescence intensity for calcium is directly proportional to concentration up to $1{\cdot}2 \times 10^{-7}M$, and the precision is ±3% for 100 ng of calcium.

The instability of BDDN in strongly alkaline aqueous solution causes a variability in fluorescence of BDDN and its metal complexes with time of standing. The instability is also influenced by absorption of ultraviolet light. Figure 3 shows that during the first 5 min of irradiation in the spectrofluorimeter, the fluorescence increases; thereafter, the gradual decomposition of the reagent and its metal complexes results in a progressive decrease in fluorescence, accompanied by a decrease in the absorption of light at the wavelength of maximum excitation. Total destruction of the naphthalene skeleton appears probable, but no study was made of the chemical character of the decomposition products. The fluorescence characteristics are not altered if the freshly prepared solution is kept for several minutes in darkness, *cf.* Fig. 3.

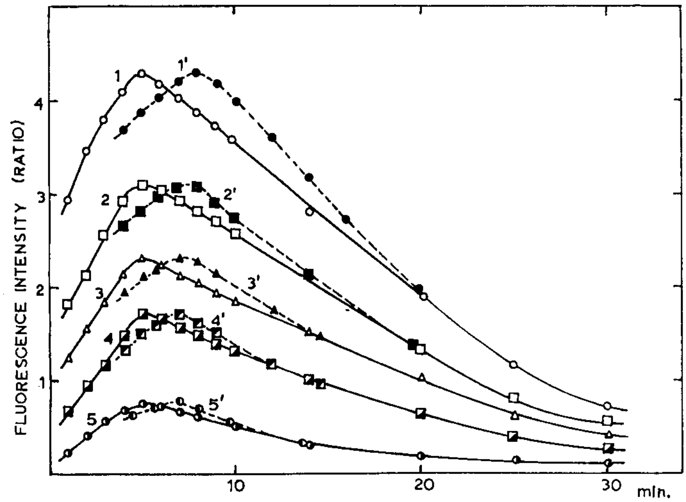


Fig. 3.—Time dependence of fluorescence of calcium (1,1′), strontium (2,2′), magnesium (3,3′) and barium (4,4′) complexes, (5,5′) reagent alone.
Curves 1, 2, 3, 4 and 5 from samples irradiated continuously in the spectrofluorimeter at 385 nm. Curves 1′, 2′, 3′, 4′ and 5′ from samples stored in darkness for the first 3 min. $C_M = 2C_L = 4{\cdot}00 \times 10^{-6}M$; pH 11·70; excitation 385 nm; emission 445 nm.

In all experiments, the temperature was 20° ± 3°. No significant variation of fluorescence with temperature of development was noted, but no specific study of the temperature effect was made.

Effect of foreign ions

The effects of 35 cations and 16 anions on the calcium determination were investigated. The tolerance limit for a foreign ion was taken as that concentration which caused an error of ±5% in the determination of 300 ng of calcium. The results obtained are summarized in Table I. The only interfering ions are magnesium (>20 ng),

TABLE I.—ANALYSIS OF CALCIUM SOLUTIONS TREATED AS UNKNOWN SAMPLES

Calcium, *ng*		
Present	Found	Foreign ions present, *ng*
10	9·5	—
50	44	—
100	102	—
200	199	—
300	295	—
400	406	—
500	501	—
200	198*	Cu(II), 6×10^5
200	195†	Fe(II), 2×105, Co(II), 2×10^5, Ni, 2×10^5
200	195*	Zn, 2×10^5, Cd, 2×10^5, Hg(II), 2×10^5
200	197*	Cu(II), 3×10^5, Ag. 3×10^5
200	194*	Sn(II), 2×10^5, Pb, 3×10^5
200	196†	Mn(II), 2×10^5, Pd(II), 3×10^5
300	297‡	Be, $1{\cdot}5 \times 10^4$
300	310‡	Be, 3×10^4
300	311‡	Be, 5×10^4
300	317‡	Be, 10^5
300	310*	Mg, 15
300	316*	Mg, 20
300	318*	Mg, 30
300	305*	Sr, 10
300	308*	Sr, 30
300	310*	Sr, 50
300	315*	Sr, 70
300	303*	Ba, 50
300	304*	Ba, 50
300	308*	Ba, 100
300	313*	Ba, 130
300	317*	Ba, 150
200	198‡	Sc 10^5, Y, 10^5, La, 10^5
200	197‡	Al, 10^5, Ga, 10^5, In, 10^5
200	195‡	Ti(IV), 10^5. Zr, 10^5, Hf, 10^5
200	196‡	Th. 2×10^5, U(IV), 2×10^5
200	195‡	V(V), 2×10^5, Nb(IV), 2×10^5. Ta(IV), 2×10^5
200	194‡	Cr(III). 2×10^5, Mo(IV), 2×10^5, W(VI), 2×10^5
300	295	$CH_3CO_2^-$, 3×10^5, Cl^-, 5×10^5
300	297	NO_3^-, 10^6, ClO_4^-, 10^7
300	294	PO_4^{3-}; 5×10^5
300	293	F^-, 3×10^5
300	294	SO_4^{2-}, 5×10^5
300	295	Br^-, 10^7, I^-, 10^7
300	295	AsO_4^{3-}, 5×10^5
300	287	tartrate, 5×10^5
300	286	citrate, 10^5
300	287	oxalate, 3×10^5
300	295	CN^-, 5×10^6
300	296	SCN^-, 5×10^6
300	286	EDTA, 120
300	281	EDTA, 200

* Masking with potassium cyanide.

† Addition of 20 mg of hydroxylamine hydrochloride to avoid aerial oxidation of Fe(II), Co(II) and Mn(II), and masking with potassium cyanide.

‡ Extraction with 8-hydroxyquinoline and masking with potassium cyanide.

strontium (>75 ng), barium (>150 ng), and EDTA (>200 ng). Other ions in amounts >100 μg do not interfere. A high sensitivity and selectivity for the determination of calcium is thus obtained.

Structure of the calcium complex

The molar ratio of metal to ligand in the complex formed was investigated by the method of continuous variation with isomolar solutions. A ratio of Ca:BDDN = 2:1 was found.

The stability constants of proton complexes of the BDDN ligand were determined over the acidity range from H^0 −4 (Hammett function) to pH 16 by ultraviolet spectrophotometry[6] at wavelengths of 220 and 230 nm. The values found are given in Table II.

TABLE II.—STABILITY CONSTANTS OF PROTON COMPLEXES OF THE LIGAND DERIVED FROM 1,5-BIS(DICARBOXYMETHYLAMINOMETHYL)-2,6-DIHYDROXYNAPHTHALENE

$\log K_1$*	13·0 ± 0·1	$\log K_5$	4·16 ± 0·05
$\log K_2$	10·4 ± 0·2	$\log K_6$	1·84 ± 0·07
$\log K_3$	8·3 ± 0·1	$\log K_7$	0·90 ± 0·05
$\log K_4$	5·3 ± 0·2	$\log K_8$	−0·15 ± 0·05

* $K_n = [H_nL]/[H_{n-1}L][H]$; charges are omitted.

The composition and overall stability constant of the calcium complex were determined by the method described elsewhere.[7,8] The values found are presented in Table III.

The structure of the fluorescent calcium complex may be of the form shown in Fig. 4*a*. The totally deprotonated ligand L^{6-}, see Fig. 4*b*, shows maximal fluorescence. These circumstances suggest that the optimum pH for fluorescence of calcium complex is about 11·7, because it is at this pH that the maximal concentration of the monoprotonated ligand HL^{5-} is available, *cf.* Table II.

TABLE III.—CONDITIONAL FORMATION CONSTANTS AND OVERALL STABILITY CONSTANTS OF CALCIUM-BDDN COMPLEX

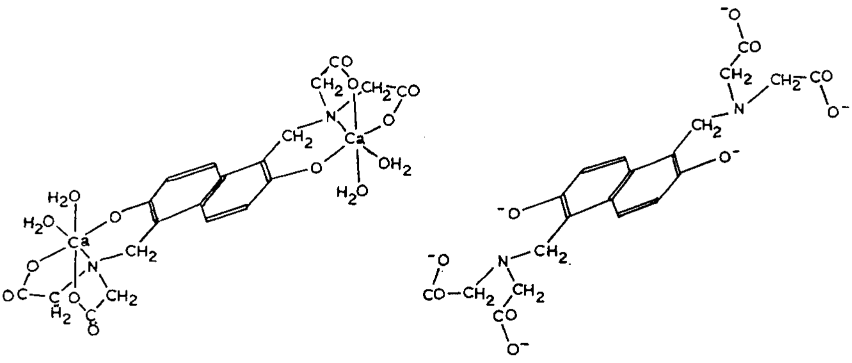
pH	F_2/F_1*	$\log K_2$	$\log \alpha_L$†(H)	$\log \beta_2$‡
12·07	2·012	13·3	1·0	14·3
11·79	2·021	12·9	1·2	14·1
11·50	2·050	12·4	1·8	14·2
10·93	2·080	12·1	2·2	14·3

* Ratio of fluorescences of solutions containing $10^{-5}M$ ligand (F_1) and $2 \times 10^{-5}M$ ligand (F_2), *cf.* ref. 7.

† $\alpha_{L(H)} = \sum_{0}^{n} [H]^n K_0 K_1 \ldots K_n$, where $K_0 = 1$.

‡ $\beta_2 = [Ca_2L]/[Ca]^2[L]$; charges are omitted.

It will be seen from Fig. 1 that whilst there are slight shifts of the maxima for excitation and fluorescence on metal complex formation, the main effect is hyperchromic. The increased efficiency of fluorescence of the metal chelate at this pH is most probably due to the removal of the last proton, leaving the fluorophore in a state similar to that of the fully ionized ligand. It is, however, true to say that the



(a) (b)

FIG. 4.—Structure of (*a*) calcium complex, (*b*) ligand.

quantum efficiency of the fully deprotonated BDDN molecule (in the absence of metal ions) is higher than that of the metal complexes.

Fluorescence of other metal ions

BDDN gives fluorescent complexes with several other ions. This property of the reagent is summarized in Table IV.

TABLE IV.—FLUORESCENCE CHARACTERISTICS OF SEVERAL METAL COMPLEXES OF BDDN

Metal ion	Optimum pH	Molar ratio metal/ligand	Wavelength maxima, *nm* excitation	emission	Relative molar fluorescence*
Be	5·8	2:1	370	405	0·99
Mg	11·7	2:1	385	445	2·30
Ca	11·7	2:1	385	445	4·31
Sr	11·7	2:1	385	445	3·08
Ba	11·7	2:1	385	445	1·73
Al	5·2	2:1	370	405	0·62

* Relative to quinine sulphate.

Conclusion

1,5-Bis(dicarboxymethylaminomethyl)-2,6-dihydroxynaphthalene is shown to be an extremely sensitive spectrofluorimetric reagent for the determination of traces of calcium down to 10 ng at a dilution limit of 1 in 10^9. Whilst the reagent and its calcium complex are unstable in solution the instability is not sufficiently marked to cause difficulties in measurement. It is also considerably better than Calcein Blue, which was previously the most sensitive-fluorimetric reagent for calcium. There is a near linear correlation between fluorescence yield and ionic radius for the alkaline earth metals. The reagent also has considerable potential for the fluorimetric determination of magnesium, and of aluminium and beryllium in acidic media where the alkaline earth metals and magnesium do not yield fluorescence.

Acknowledgements—We are grateful to the Czechoslavek Academy of Sciences for granting study leave to one of us (B. B.) and to the Science Research Council for a grant for the purchase of the spectrofluorimeter used in those studies.

Zusammenfassung—1,5-Bis(dicarboxymethylaminomethyl)-2,6-dihydroxynaphthalin (BDDN) bildet fluoreszenzfähige Komplexe mit Aluminium, Barium, Beryllium, Calcium, Magnesium und Strontium. Alle Komplexe haben das Metall:Ligand-Verhältnis 2:1. Barium, Calcium, Magnesium und Strontium zeigen die maximale Fluoreszenz bei pH 11,7 mit Anregungs- und Emissionsmaxima bei 385 bzw. 445 nm. Aluminium und Beryllium zeigen maximale Fluoreszenz bei pH 5,8 bzw. 5,2; die Anregungs- und Emissionsmaxima liegen bei 370 bzw. 405 nm. Die Bildung des Calciumkomplexes erlaubt ein sehr empfindliches und selektives Analysenverfahren für Calcium im Bereich 10–500 ng. Die Fluoreszenzmessung von Calcium sollte innerhalb 5 min nach) Mischen der Lösungen ausgeführt werden, da beim angegebenen pH das Reagens instabil ist. Kaliumcyanid kann als Maskierungsmittel verwendet werden; drei- und vierwertige Kationen sollte man durch vorausgehende Extraktion mit 8-Hydroxychinolin in Chloroform bei pH 6,0 entfernen. Unter diesen Bedingungen störten unter 33 untersuchten Kationen nur Magnesium (>20 ng), Strontium (>70 ng) und Barium (>150 ng) bei der Bestimmung von 300 ng Calcium. Von 16 untersuchten Anionen störte nur EDTA wesentlich.

Résumé—Le 1,5-bis(dicarboxyméthylaminométhyl)2,6-dihydroxynaphtalène (BDDN) forme des complexes fluorescents avec l'aluminium, le baryum, le beryllium, le calcium, le magnésium et le strontium. Tous les complexes sont 2:1 métal:ligand. Baryum, calcium magnésium et strontium offrent une fluorescence maximale à pH 11,7 avec les maximums d'excitation et d'émission à 385 et 445 nm respectivement. L'aluminium et le beryllium montrent une fluorescence maximale à pH 5,8 et 5,2 respectivement, les maximums d'excitation et d'émission étant à 370 et 405 nm. La formation du complexe calcique apporte un dosage hautement sensible et sélectif du calcium dans le domaine 10–500 ng. La mesure de fluorescence du calcium doit être effectuée dans les 5 mn qui suivent le mélange des solutions par suite de l'instabilité du réactif au pH donné. On peut utiliser le cyanure de potassium comme agent de dissimulation, et les cations tri- et tétravalents doivent être éliminés par extraction préliminaire à la 8-hydroxyquinoléine en chloroforme à pH 6,0. Dans de telles conditions, des 33 cations étudiés, seuls les magnésium (>20 ng), strontium (>70 ng) et baryum (>150 ng) apportent une gêne dans le dosage de 300 ng de calcium. Parmi 16 anions examinés, seul l'EDTA interfère sérieusement.

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SHORT COMMUNICATIONS

Phosphorescence characteristics of several antimetabolites

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PHOSPHORIMETRY has become widely accepted as an analytical tool for the study and analysis of compounds of biochemical interest.[1] It has previously been used to determine the nicotine alkaloids in tobacco,[2] drugs in biological fluids,[3-7] and pesticides in foods and in biological fluids.[8,9] In this study, the phosphorescence characteristics of 37 antimetabolites were determined, and the possible application of phosphorimetric techniques to the determination of 17 of these compounds in biological materials is indicated. The antimetabolites studied are of considerable importance in plant and animal growth.

EXPERIMENTAL

Apparatus

All phosphorimetric measurements were taken with the Aminco Bowman spectrophotofluorometer (No. 4-8202) with the phosphoroscope attachment (No. C 27-62140) and a xenon lamp (No. 901 C-1; all items manufactured by American Instrument Company, Inc., Silver Spring, Maryland). All studies were made with the slit programme: A 4 mm, B 3 mm, C 3 mm, D 4 mm and E 3 mm. All spectra were recorded with an Aminco X–Y recorder (No. 1620-827, American Instrument Company, Inc.)

Reagents

All antimetabolites were purchased in a growth factor analogue kit (Nutritional Biochemicals Corporation, Cleveland, Ohio). Absolute ethanol (Union Carbide Corporation) purified as previously described,[4] was used as the solvent for all phosphorimetric measurements. Stock ethanolic solutions (approximately $10^{-3}M$) of each compound were prepared. Solutions of lower concentrations were prepared by successive dilution. Ethanol was used as the solvent because it is inexpensive, can be prepared in a highly pure state, and freezes to a clear, rigid glass at 77°K.

Procedures

Analytical curves (logarithm of phosphorimetric signal *versus* logarithm of concentration) were obtained to determine whether a compound was analytically useful, and its limit of detection. The limit of detection was defined[10] as the concentration which gave a signal-to-noise ratio of $t\sqrt{2}/\sqrt{n}$. The noise was estimated to be one fifth of the range of fluctuation in the background signal, t was the Student t, and n was the number of combined blank and sample measurements made at the limit of detection. With n equal to six and a 99% confidence level, the signal-to-noise ratio is approximately 2.

The lifetime, τ, was measured by terminating the exciting radiation with a manual shutter and plotting the phosphorimetric signal *versus* time with the X–Y recorder. The response of the recorder prevented any τ measurements shorter than 0·5 sec.

RESULTS AND DISCUSSION

Seventeen antimetabolites having analytically useful phosphorescence are given in Table I. In addition to these 17 compounds, barbituric acid, gamma hexachloro benzene, DL-*p*-fluorophenylalanine, pyridine-3-sulphonic acid, β-2-thienylalanine, β-2-thienylserine, and DL-β-3-thienylalanine phosphoresced, but too weakly to be considered analytically useful. The remaining 12 antimetabolites did not phosphoresce [allylglycine, aminoacetic acid (glycine), L-arginine hydrochloride, L-asparagine, L-canavanine sulphate, desthiobiotin, dihydrocholesterol, DL-leucine, D-leucine, DL-methionine sulphoxide, DL-α-methylglutamic acid and sodium salt of pantoyl taurine].

The limits of detection of the antimetabolites listed in Table I compare favourably with those attained by currently accepted colorimetric (0·1–1 μg/ml) and enzymic (0·01–0·1 μg/ml) procedures. Previous studies of conjugated ring system analogues showed that phosphorecence could be enhanced

TABLE I.—PHOSPHORIMETRIC CHARACTERISTICS OF SEVERAL ANTIMETABOLITES

Antimetabolite	Excitation maximum,*† *nm*	Emission maximum*†, *nm*	Limit of detection, *μg/ml*	Lifetime‡ *sec*	Concentration range of near linearity
3-Acetylpyridine	277	424	3·6	<0·5	10^4§
Adenosine	280	422	0·80	3·2	10^1§
2-Amino-4-methylpyrimidine	302	438	0·033	2·1	10^3§
L-3-3Aminotyrosine dihydrochloride	286	398	0·81	2·4	10^2§
8-Azaguanine	282	442	0·30	1·8	10^2§
Benzimidazole	280	406	0·0059	2·3	10^4§
2-Chloro-4-aminobenzoic acid	312	447	0·069	1·0	10^2
Desoxypyridoxine hydrochloride	290	442	0·076	1·4	10^3
2,6-Diaminopurine sulphate	294	424	1·2	1·7	10^2§
Estradiol	292	403	0·29	2·0	10^3§
Oxythiamine hydrochloride	272	460	3·4	<0·5	10^2§
DL-β-Phenyl-lactic acid	262	383	5·0	5·4	10^2§
α-Picolinic acid hydrochloride	278	400	0·014	5·2	10^3
Pyridine-3-sulphonic acid (Na salt)	272	408	4·8	1·2	10^2§
Quercetin	343	480	0·30	2·1	10^3§
Sulphanilamide	297	411	0·012	2·9	10^5§
2-Thiouracil	312	432	0·0038	<0·5	10^4§

* Peaks are uncorrected for instrumental characteristics.

† Relative error of ±5nm in wavelength of peaks.

‡ Limiting value of lifetime (0·5 sec) is determined by recorder response time.

§ Upper concentration $(10^{-3}M)$ is still on linear portion of analytical curve. Therefore actual range will be greater than that reported.

by selective substitution on the ring(s) with corresponding improvement of the limits of detection. Therefore, values for limits of detection found in Table I indicate promise and need for further work on analogues of pharmacological interest.

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Summary—Phosphorescence excitation and emission wavelength peaks, lifetimes, limits of detection, and concentration ranges of analytical usefulness of 37 antimetabolites in rigid (77°K) ethanolic solution were determined. Seventeen of the metabolites produced analytically useful phosphorescence, whereas the remaining 20 were of limited or no analytical use.

Zusammenfassung—Die Wellenlängen der Anregungs- und Emissionsmaxima der Phosphoreszenz, Lebensdauern, Nachweisgrenzen und analytisch nutzbare Konzentrationsbereiche von 37 Antimetaboliten in glasartiger (77°K) äthanolischer Lösung wurden ermittelt. Siebzehn der Metaboliten zeigen analytisch nutzbare Phosphoreszenz, die übrigen 20 waren von beschranktem oder keinem analytischen Nutzen.

Résumé—On a déterminé les longueurs d'onde des maximums d'excitation et d'émission de phosphorescence, les durées de vie, les limites de détection et les domaines de concentration d'utilité analytique pour 37 antimétabolites en solution éthanolique rigide (77°K). Dix sept des métabolites produisent une phosphorescence analytiquement utile, tandis que les 20 restant sont d'emploi analytique limité ou nul.

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Separation of zirconium by thin-layer chromatography

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Reversed-phase thin-layer chromatography has been used for the separation of zirconium,[1-3] but normal-phase thin-layer chromatography has scarcely been used. Galiardi and Pokorny[4] separated Zr(IV), Ni(II), Al(III), Ti(IV), Mn(II), Cd(II), V(V), U(VI), Fe(III) and Zn(II) by development with acetone–6*M* hydrochloric acid–dioxan or ethyl methyl ketone on silica gel layers. Breccia and Spalletti[5] separated zirconium-95 and niobium-95 by eluting with methanol–10*M* hydrofluoric acid (25:1) on silica gel layers. Moghissi[6] separated these radionuclides by eluting with 0·25*M* oxalic acid and 0·1*M* hydrochloric acid in ethyl methyl ketone, dioxan and water (5:1:1) on Kieselguhr or Kieselgel layers.

The present work was, therefore, undertaken to provide more simple and effective TLC systems for the separation involving Zr, Sc, Y, Th, U(VI), rare earth and other metal ions. Zirconium remains at the starting point on silica gel–cellulsoe (5:1) plates in mesityl oxide–ethanol–nitric acid media, whilst 19 of the other metal ions tested have larger R_f values, except silver, which tails. This forms the basis of a very selective method for the separation of zirconium.

EXPERIMENTAL

Reagents

Test solutions of metal ions, 0·1*M*. Appropriate amounts of the nitrates of U(VI), Th, Al, Pb, Co(II) and Ag were dissolved in 1*M* nitric acid.

Appropriate amounts of the oxides or carbonates of Fe(III), Zn, Cd, Cu(II), Ni, Sc, Y, La, Sm, In, Bi(III), Hg(II), Mg and Ca were converted into the nitrate by treatment with excess of nitric acid, followed by evaporation to dryness. The resulting nitrates were dissolved in 1*M* nitric acid.

Zirconyl chloride was dissolved in dilute nitric acid and the solution made ammoniacal. The precipitate of zirconium hydroxide was filtered off and washed free from chloride with demineralized water, and dissolved in nitric acid. The solution was evaporated to dryness and the residue dissolved in 1*M* nitric acid.

Preparation of thin-layer plates. Silica gel (25 g, WAKOGEL B-O, Wako Pure Chemical Industries Co. Ltd., Osaka, Japan) purified according to Seiler's method,[7] and cellulose powder MN-300 (5 g, Machery, Nagel Co., Ltd., Düren, Germany) were mixed thoroughly with 87 ml of demineralized water. The slurry was spread 250 μ thick on 100 × 100 mm or 200 × 200 mm glass plates. The thin-layer plates were dried first in air for 1 hr and then in an oven at 105–110° for 1 hr and were stored in a desiccator till used.

TABLE I.—R_f VALUES FOR ZIRCONIUM, SCANDIUM, YTTRIUM, LANTHANUM, SAMARIUM, THORIUM AND URANIUM(VI) IN VARIOUS SOLVENT SYSTEMS

Solvent systems	R_f values						
	Zr	Sc	Y	La	Sm	Th	U(IV)
1. M.O.-1*M* HNO_3*	0·00–0·03	0·00–0·84	0·00–0·78	0·00–0·47	0·00–0·70	0·00–0·94	0·42–1·00
2. M.O.-3*M* HNO_3*	0·00–0·05	0·10–0·81	0·00–0·36	0·00–0·21	0·00–0·34	0·30–1·00	0·80–1·00
3. M.O.-5*M* HNO_3*	0·00–0·06	0·21–0·67	0·00–0·25	0·00–0·20	0·00–0·26	0·55–1·00	0·84–1·00
4. M.O.-EtOH-1*M* HNO_3 (3:4:3)	0·00–0·07	0·80–0·96	0·76–0·92	0·76–0·92	0·77–0·92	0·57–0·91	0·86–1·00
5. M.O.-EtOH-3*M* HNO_3 (3:4:3)	0·00–0·06	0·85–0·97	0·68–0·86	0·62–0·82	0·63–0·85	0·46–1·00	0·88–1·00
6. M.O.-EtOH-5*M* HNO_3 (3:4:3)	0·00–0·06	0·86–0·96	0·62–0·75	0·60–0·77	0·62–0·78	0·60–1·00	0·91–1·00
7. M.O.-EtOH-1*M* HNO_3 (5:3:2)	0·00–0·04	0·74–0·93	0·52–0·77	0·48–0·75	0·53–0·77	0·32–1·00	0·87–1·00
8. M.O.-EtOH-3*M* HNO_3 (5:3:2)	0·00–0·05	0·80–0·92	0·36–0·66	0·38–0·70	0·42–0·72	0·63–1·00	0·87–1·00
9. M.O.-EtOH-5*M* HNO_3 (5:3:2)	0·00–0·06	0·77–0·96	0·35–0·66	0·38–0·66	0·39–0·67	0·70–1·00	0·81–1·00
10. M.O.-3*M* HNO_3-3*M* $NaNO_3$*	0·00–0·03	0·11–0·42	0·00–0·07	0·00–0·07	0·00–0·07	0·00–1·00	0·90–1·00
11. M.O.-1*M* HNO_3-5*M* $NaNO_3$*	0·00–0·02	0·00–0·41	0·00–0·06	0·00–0·06	0·00–0·06	0·00–0·92	0·47–0·94

Mesityl oxide is abbreviated as M.O. and ethyl alcohol as EtOH.

* Mesityl oxide was vigorously shaken with half its volume of nitric acid or nitrate solution in a separating funnel for 1 min. Then the two phases were separated and the organic phase was used as developing solvent.

Time of development: solvents 1–3, 20 min; solvents 4–6, 50 min; solvents 7–9, 40 min; solvents 10, 11 and 20 min.

Procedure

About 0·5 μl of each test solution was spotted with a micro pipette at 25 mm from one end of the plate. The spots were air-dried for ~30 min, but drying for up to 45 min did not affect the reproducibility of R_f values. The plates were inserted in the tanks, which had already been conditioned with solvent vapour for 10 min, and immediately developed (100-mm solvent travel) by the ascending technique at room temperature. The developing solvents used are listed in Table I. The plates were then air-dried and the metal ions detected as follows.

Arsenazo III, 1% solution; U(VI), Th, Sm, La, Zr, Y and Sc were detected as green spots on a pink background.

Ammonium sulphide, dilute colourless solution; Bi(III), Hg(II), Pb, Ni, Cu(II), Co(II) and Ag formed coloured spots.

8-*Hydroxyquinoline*, 1% solution in ethanol, followed by exposure to ammonia; Mg, Ca, Al, Fe(III), Zn, Cd and In showed up in UV light.

All R_f values are given for the leading and trailing edges of the spots.

RESULTS AND DISCUSSION

Table I shows R_f values for Zr, Sc, Y, La, Sm, Th and U(VI) in various solvent systems. Zirconium remains stationary in all systems. Tailing is dependent on nitric acid concentration in some systems (esp. 1–3, Sc).

Khopkar and Dhara[8] reported that the presence of ammonium and sodium nitrate in the aqueous phase increased the extraction of zirconium with 100% mesityl oxide in the acidity range 2·5–4*N*, but it is clear that the salting-out effect does not affect the developing process in this system.

Twenty-one metal ions including those described above were chromatographed in mesityl oxide–ethanol–5*M* nitric acid (5:3:2) and in mesityl oxide–5*M* nitric acid, and the additional results are summarized in Table II. The results show that it should be possible to resolve several 2–4 ion mixtures and this was confirmed experimentally for 29 mixtures.

TABLE II.—R_f VALUES FOR METAL IONS, NOT INCLUDED IN TABLE I

Metal ion	Mesityl oxide–5*M* HNO_3	Mesityl oxide–ethanol–5*M* HNO_3 (5:3:2)
Bi(III)	0·81–1·00	0·84–1·00
Cu(II)	0·00–0·10	0·53–0·71
Hg(II)	0·88–1·00	0·90–1·00
Pb(II)	0·00–0·10	0·35–0·51
Co(II)	0·00–0·06	0·42–0·65
Ni(II)	0·00–0·03	0·39–0·60
In(III)	0·03–0·13	0·64–0·85
Mg(II)	0·00–0·05	0·45–0·65
Cd(II)	0·02–0·09	0·55–0·71
Zn(II)	0·00–0·06	0·39–0·66
Fe(III)	0·00–0·06	0·42–0·71
Al(III)	0·00–0·03	0·48–0·75
Ca(II)	0·00–0·05	0·46–0·62
Ag(I)	0·00–0·45	0·00–0·74

Zirconium is separated from nineteen of the ions tested in mesityl oxide–ethanol–5*M* nitric acid (5:3:2), but not from silver. In order to be useful this separation of zirconium and other metal ions should include varying ratios of zirconium and other metal ions. This was verified experimentally for 100:1 and 1:100 mixtures of Zr and either Fe, In, Co, Si, La, Th or U.

General remarks

Mesityl oxide was found to be gradually decomposed by nitric acid, so that nitric acid >5*M* was not used.

The mixture of silica gel and cellulose formed thin layers that were more stable during handling and brought about better separation more rapidly than the mixture of silica gel and starch which is generally used in inorganic thin-layer chromatography.

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Summary—The thin-layer chromatographic separation of a number of metal ions [Sc, Y, Zr, La, Sm, Th, U(VI), *etc.*] with solvent mixtures of mesityl oxide, ethanol and 5*M* nitric acid on silica gel–cellulose (5:1) thin-layer plates is reported. Zirconium remains stationary whilst the other metal ions move with the solvent, thus allowing a selective separation of zirconium from about 20 metal ions in ratios ranging from 100:1 to 1:100. Mixtures of various metal ions can also be separated.

Zusammenfassung—Die dünnschichtchromatographische Trennung einer Anzahl von Metallionen [Sc, Y, Zr, La, Sm, Th, U(VI) usw.] mit Lösungsmittelgemischen von Mesityloxid, Äthanol und 5*M* Salpetersäure auf Dünnschichtplatten aus Silicagel-Cellulose (5:1) wird mitgeteilt. Zirkonium bleibt stehen, während die anderen Metallionen mit dem Lösungsmittel wandern. Damit ist eine Abtrennung von Zirkonium von etwa 20 Metallionen in Mengenverhältnissen zwischen 100:1 und 1:100 möglich. Gemische verschiedener Metallionen können ebenfalls getrennt werden.

Résumé—On rapporte la séparation chromatographie sur couche mince d'un certain nombre d'ions métalliques [Sc, Y, Zr, La, Sm, Th, U(VI), etc.] avec des mélanges solvants d'oxyde de mésityle, éthanol et acide nitrique 5*M* sur des plaques à couches minces de gel de silice–cellulose (5:1). Le zirconium reste stationnaire tandis que les autres ions métalliques se déplacent avec le solvant, permettant ainsi une séparation sélective du zirconium d'environ 20 ions métalliques dans des rapports allant de 100:1 à 1:100. On peut aussi séparer des mélanges de divers ions métalliques.

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A highly sensitive extraction–photometric method for nickel with dithizone and phenanthroline

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ALTHOUGH diphenylthiocarbazone (dithizone) serves as an extractant and highly sensitive colorimetric reagent for many transition and heavy metal ions, it has not been found useful for determining nickel Ref. (1). Two reasons for this are (*a*) the spectrum of the nickel chelate is rather complex and does not contain an absorption band of comparable intensity to those of other metal ions and (*b*) the rate of formation of the nickel complex is so slow that equilibration may require over an hour of shaking.

During the course of an investigation of adduct and mixed ligand chelate extraction systems, we found that the addition of heterocyclic nitrogen bases such as pyridine and phenanthroline to a chloroform solution of dithizone gave rise to a reagent which was free from the disadvantages of dithizone used alone. Nickel was rapidly and quantitatively extracted over a broad pH range (from 5·5 to at least 11·0) to give a very highly coloured mixed ligand complex having an absorption band centred at 520 nm. The mixed ligand complex is sufficiently stable to permit the removal of excess of dithizone by back-extraction with 0·1*M* sodium hydroxide, so a "monocolour" method is applicable. The molar absorptivity of this complex is $49{\cdot}1 \times 10^3$, which makes a method based on this reaction about four times as sensitive as the currently most sensitive method, that using dimethylglyoxime and an oxidizing agent.[2]

Procedure

To 10 ml of a solution containing from 1 to 10 μg of nickel (up to 25 μg may be accommodated), add 5 ml of a phthalate or acetate buffer of pH 6·0 (or dilute ammonia may be used) followed by 15 ml of a chloroform solution $7 \times 10^{-5}M$ in dithizone and $3 \times 10^{-5}M$ in phenanthroline. Shake the phases for 5 min, allow them to settle, and separate them. Back-extract the chloroform layer with 10 ml of 0·1*M* sodium hydroxide by vigorous shaking for about 1 min. Read the absorbance of the chloroform extract in a 10-mm cell at 520 nm against a similarly treated blank. Construct a calibration curve (a straight line passing through the origin and having a slope of $49{\cdot}1 \times 10^3$ l. mole^{-1}. cm^{-1}). Typical results are tabulated below.

Ni taken, μg	Absorbance at 520 nm	Ni found, μg
1·41	0·078	1·43
4·93	0·285	5·08
7·05	0·383	6·87
8.46	0·487	8·74

The extraction of the mixed ligand complex does not in itself provide a significant increase in selectivity over the extraction by dithizone. It should be possible, if desired, to make use of the much slower rate of nickel dithizonate extraction,[3] however, to provide separation from zinc and perhaps cobalt, before the addition of phenanthroline.

An equilibrium study of the reaction of the adduct and mixed ligand complexes formed from various heterocyclic nitrogen bases and dithizone will be published elsewhere.

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Summary—Addition of phenanthroline to nickel dithizonate in chloroform results in a mixed ligand complex, NiDz$_2$phen, the high molar absorptivity of which (49.1×10^3) results in a colorimetric estimation of nickel that is significantly more sensitive than any other method.

Zusammenfassung—Die Zugabe von Phenanthrolin zu Nickel-Dithizonat in Chloroform liefert den gemischten Komplex NiDz$_2$phen, dessen hoher molarer Extinktionskoeffizient ($49{,}1 \cdot 10^3$) eine Möglichkeit zur kolorimetrischen Bestimmung von Nickel bietet, die wesentlich empfindlicher als alle anderen ist.

Résumé—L'addition de phénanthroline au dithizonate de nickel en chloroforme mène à un complexe ligand mixte, NiDz$_2$phen, dont le coefficient d'absorption moléculaire élevé ($49{,}1 \times 10^3$) conduit à un dosage colorimétrique du nickel qui est notablement plus sensible que n'importe quelle autre méthode.

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Spectrophotometric determination of copper in plutonium metal with 2,9-dimethyl-1,10-phenanthroline*

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EMISSION spectroscopy is commonly used for the determination of impurities in plutonium. Other methods for the determination of individual elements, however, are extensively used when the verification of spectrographic results is required.

In the past, the method used in the Rocky Flats Plant Plutonium Laboratory was based on the work of Lindsay.[1] The plutonium metal was dissolved in 6*M* hydrochloric acid–1% ascorbic acid, and separated on anion-exchange resin with subsequent elution of copper with 3*M* ammonia. The copper was determined spectrophotometrically as the 1,10-phenanthroline complex. This method proved unsuitable because of the production of ammonium chloride which coated the glove-box windows and filters, and because it was too time-consuming.

A new analytical method for determining trace amounts of copper in plutonium was needed. A solvent extraction–spectrophotometric procedure was desired because of the speed and reproducibility of such a procedure and because of the previous success with such a procedure for iron.[2]

Work of several investigators[3–6] had revealed that trace amounts of copper could be determined in a variety of matrices with neocuproine, bis(2,9-dimethyl-1,10-phenanthroline). The reagent was reported to be specific for copper.[3] The application of this reagent for the determination of copper in plutonium appeared to be the best approach to the problem if a suitable solvent extraction technique could be developed. The results are described in this paper.

After the work on this problem had begun, a report appeared which described the separation and determination of copper and plutonium by solvent extraction with pentanol.[7]

EXPERIMENTAL

Safety precautions

Because of the toxicity of plutonium, extreme care must be exercised in its handling. All work with plutonium was performed in glove-boxes.

Reagents

Two copper standards of 200 and 100 μg/ml were prepared from 99·90% copper metal dissolved in 6*M* nitric acid and diluted to volume with distilled water. A 0·1% solution of neucuproine was prepared by dissolving the hemihydrate in ethanol.

Sample preparation

A weight of plutonium metal was selected so that 20–200 μg of copper were present. This sample was dissolved in a minimum amount (2–4 ml) of 6*M* hydrochloric acid. After dissolution, 5 ml of 10% hydroxylamine hydrochloric were added, followed by 10 ml of water and 10 ml of 30% sodium citrate dihydrate solution. The citrate was added to prevent hydrolysis of the plutonium and to buffer the solution. Then 5ml of neocuproine solution were added, followed by 25 ml of chloroform from an automatic filling and dispensing pipette. The mixture was shaken vigorously for approximately 30 sec, and the two phases were permitted to separate. Five ml of ethanol were added to a dry 25-ml volumetric flask from an automatic filling and dispensing pipette, and the flask was filled to volume with the chloroform extraction layer. The ethanol enhances the colour of the copper–neocuproine complex. The chloroform–ethanol mixture was then transferred to a 10-mm silica cell, and the absorbance was determined at 457 mμ against a reagent blank as the reference solution.

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A calibration curve was prepared over the range 20–200 μg/25 ml of chloroform and was found to be linear and to pass through the origin when extrapolated. The relative standard deviation of the slope was 4% (8 copper concentrations).

RESULTS AND DISCUSSION

It was found that over the pH range 3–9 the copper recovery was essentially 100%, decreasing at higher and lower pH values. This pH range agreed with previous work.[6] The colour of the complex was stable for at least 4 hr.

Since a pH of 3–9 was required for optimum extraction of the copper–neocuproine complex, it was necessary to complex the plutonium to prevent its hydrolysis during the extraction. A number of complexing agents were tried, and citrate was found to be the most efficient. No hydrolysis was observed if 10 ml of a 30% sodium citrate solution were added to samples containing up to 1 g of plutonium. It was also found that the sodium citrate would buffer the solution within the optimum pH range if a minimum amount of acid was used to dissolve the plutonium.

The major impurities, at their maximum concentrations, that are found in plutonium metal, together with several anions commonly encountered in the analysis of plutonium compounds, were investigated to determine what effect they might have on the determination of copper. The results, shown in Table I, indicate that there is no serious interference by these 13 ions.

TABLE I.—EFFECT OF DIVERSE IONS ON THE RECOVERY OF 100 μg OF COPPER

Impurity		Cu found, μg
Ion	*mg*	
Al^{3+}	0·4	99
Cr^{3+}	0·4	102
Fe^{3+}	0·5	100
Ga^{3+}	0·5	101
Mg^{2+}	0·2	99
Mo^{6+}	0·3	101
Ni^{2+}	0·5	100
Pb^{2+}	0·4	100
U^{6+}	0·5	100
Zn^{2+}	0·3	100
F^-	2·0	102
NO_3^-	5·0	101
SO_4^{2-}	5·0	100

TABLE II.—RECOVERY OF COPPER FROM SYNTHETIC PLUTONIUM SAMPLES

Cu, μg		Recovery, %	Relative standard deviation, %
Added	Found*		
25	24	96	3·1
50	50	100	2·0
100	98	98	1·6
150	149	99	2·4
200	199	99	2·2

* Mean of six results.

The effect of plutonium on the spectrophotometric determination of copper, as the neocuproine complex, was determined by spiking plutonium solutions with standard copper solutions. These solutions, containing 300 mg of plutonium and 25–200 μg of copper were analysed by the procedure given and the results are shown in Table II. The average recovery from the 30 samples, six for each copper concentration, was 98·6% the range being 93–102%.

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Summary—A spectrophotometric method for the determination of copper plutonium has been developed. The copper is complexed with neocuproine, extracted into chloroform, and the absorbance read at 457 mμ. The average relative error of the method is −1·4% with an average relative standard deviation of 4%.

Zusammenfassung—Ein spektrophotometrisches Verfahren zur Bestimmung von Kupfer in Plutonium wurde entwickelt. Das Kupfer wird in den Neocuproinkomplex überführt, in Chloroform extrahiert und die Extinktion bei 457 mμ abgelesen. Der mittlere relative Fehler der Methode beträgt −1,4% mit einer mittleren relativen Standardabweichung von 4%.

Résumé—On a élaboré une méthode spectrophotométrique de dosage du cuivre dans le plutonium. On complexe le cuivre par la néocuproïne, l'extrait en chloroforme et lit l'absorption à 457 mμ. L'erreur relative moyenne de la méthode est de −1,4% avec un écart type relatif moyen de 4%.

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Spectrophotometric determination of selenium with cyclohexanone

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THE application of the reaction of selenium(IV) with aliphatic monoketones to the solvent-extraction separation of selenium has recently been examined by Jordanov and Futekov[1,2] and by Gotô and Kakita.[3] These workers extracted the selenium ketone–chloro complexes into the ketones from hydrochloric acid solution. The reaction, which is used in preparative organic chemistry as a selective oxidation procedure, results in formation of elemental selenium if it is allowed to proceed beyond the formation of the intermediate complex. The reaction is applied here to the spectrophotometric determination of selenium in the range 0·05–10 ppm, and because selenium(VI) is rapidly reduced to selenium(IV) under the conditions employed, the initial oxidation state of the element is not important, an unusual advantage for a spectrophotometric procedure.

EXPERIMENTAL

Reagents

Selenium(IV) *solution* (100 *μg/ml*). Dissolve 0·100 g of analytical reagent grade selenium powder in 5 ml of concentrated hydrochloric acid and 1ml of concentrated nitric acid. Warm to aid dissolution, and heat gently to expel brown fumes. Because nitrate must be removed completely, it is advisable to add 1 ml of concentrated sulphuric acid to prevent loss of selenium chloride. Cool and dilute to 1 litre.

Selenium(VI) *solution* (100 *μg/ml*). Dissolve 0·227 g of ammonium selenate in water, and dilute to 1 litre.

Procedure

Transfer by pipette 0·02–1 ml (2–100 μg) of stock selenium(IV) or (VI) solution into a series of 10-ml graduated flasks. Add cyclohexanone (0·1 ml) and concentrated hydrochloric acid (6·0 ml) and dilute to volume with distilled water. Pour the resulting solutions into test-tubes, warm for 5 min in a boiling water-bath, cool under cold running water, and measure the absorbance at 345 nm, in 10-mm cells, against a reagent blank prepared under identical conditions. Plot a calibration curve.

Treat samples (containing <100 μg of selenium in ≯3·9 ml) in the same way. If metals are present which form chloro-complexes which absorb at 345 nm, measure against a distilled water blank the absorbance of a sample prepared as above but without the addition of cyclohexanone, and subtract it from the absorbance obtained by the normal procedure. This method can be used to determine 10 μg of selenium in the presence of 100 μg of iron(III), 5 mg of cobalt(II) or 500 μg of copper(II).

Tellurium interferes with the reaction and must be removed, *e.g.*, by extraction with tribenzylamine into chloroform.[4,5] Oxidizing agents such as nitrate interfere and must be removed (nitrate can be removed by heating to fumes in the presence of a small amount of sulphuric acid). Reducing agents such as sulphite, iodide and tin(II) also interfere, and must be oxidized with an easily removable oxidizing agent such as bromine water.

RESULTS AND DISCUSSION

The absorption spectrum is shown in Fig. 1. The dependence of the absorbance at 345 nm on the acid concentration is shown in Fig. 2. This shows that the hydrochloric acid concentration must be carefully controlled.

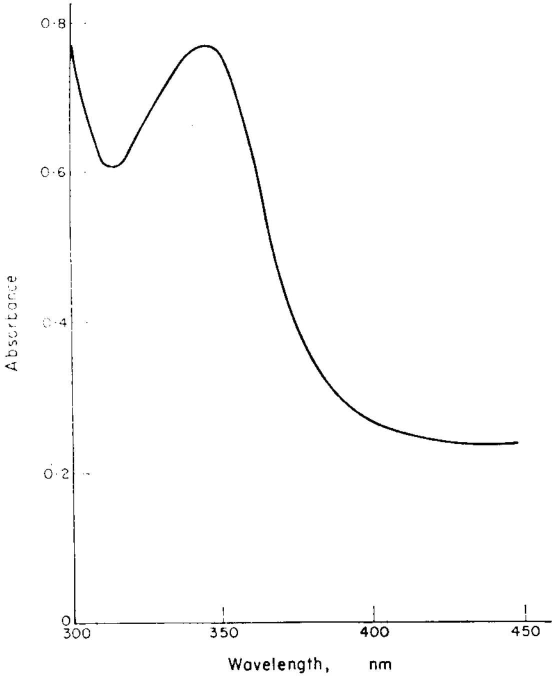

FIG. 1.—Absorption spectrum.
100 μg selenium;
10-mm cuvettes; *vs.* reagent blank.

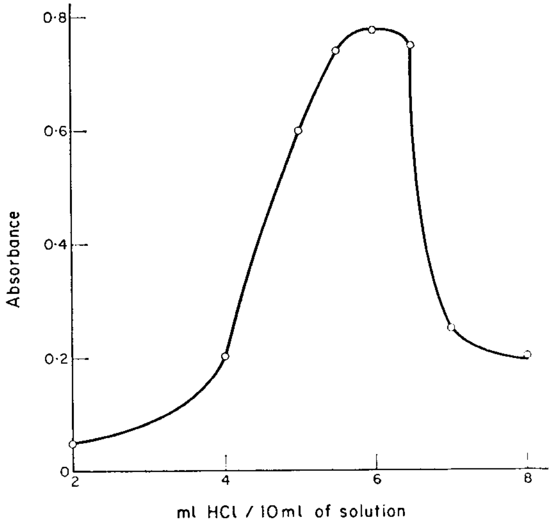

FIG. 2.—Effect of acid concentration.

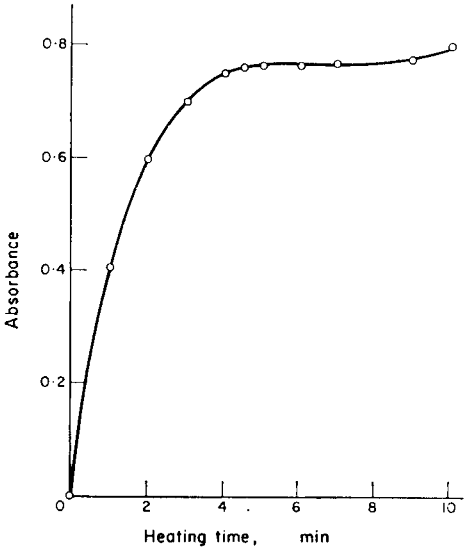

FIG. 3.—Effect of heating time.

At room temperature the reaction is only complete after 18 hr and the wavelength of maximum absorption shifts to 375 nm. At the temperature employed here, however, the reaction is complete in 5 min. The effect of heating time is shown in Fig. 3. After formation, the absorbance remains constant for at least 2 hr.

The wavelength of maximum absorption increases steadily as the ketone concentration is increased, whereas the maximum absorbance increases only slightly. A volume of 0·1 ml of cyclohexanone per 10 ml of solution was finally selected, because higher concentrations of ketone gave rise to turbid solutions and a much lower precision.

The calibration curve is linear in the range 0·05–10 ppm, and the extinction coefficient at 345 nm is $5{\cdot}6 \times 10^3$. The relative standard deviation (10 variates) was 50%, 1·8%, and 1·3% at 0·05, 1, and 5 ppm of selenium respectively.

Interferences

A 200-fold excess of the following ions caused less than 3% error in the determination of 1 ppm of selenium: Li^+, Na^+, K^+, NH_4^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, F^-, Cl^-, Br^-, SO_4^{2-}, oxalate, citrate, tartrate. Of the ions tested, Fe^{3+}, Cu^{2+} and Co^{2+} interfere because of the absorbance of their chloro-complexes at 345 nm. Oxidants, reductants and tellurium interfere and must be removed beforehand. The results obtained for some synthetic samples are shown in Table I.

TABLE I.— DETERMINATION OF Se IN PRESENCE OF INTERFERING IONS

Se taken, μg	Interfering ion	Se found, μg	Error
10	100 μg Fe^{3+}	9·8	−2%
10	100 μg Cu^{2+}	10·3	+3%
10	250 μg Cu^{2+}	10·4	+4%
10	1 mg Co^{3+}	9·9	−1%
10	2 mg Co^{3+}	9·8	−2%
10	500 μg Te^{4+}	9·8	−2%

Acknowledgement—We are grateful to the Agricultural Research Council for financial aid in support of this work.

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Summary—Selenium (2–100 μg) can be determined directly in the aqueous phase by formation of the ketone–chloro complex with cyclohexanone in ~7M hydrochloric acid from either selenium(IV) or selenium(VI), the reaction being brought to completion by heating for 5 min in a boiling water-bath.

Zusammenfassung—Selen (2–100 μg) kann direkt in der waßrigen Phase bestimmt werden. Aus Selen(IV) oder Selen(VI) bildet sich in ca. 7 M Salzsäure mit Cyclohexanon ein Keton-Chlorokomplex. Die Reaktion ist nach 5 Minuten Erhitzen in einem siedenden Wasserbad beendet.

Résumé—On peut doser le sélénium (2–100 μg) directement en phase aqueuse par formation du complexe chloro-cétonique avec la cyclohexanone en acide chlorhydrique ~7 M à partir du sélénium(IV) ou du sélénium(VI), la réaction étant conduite à bonne fin par chauffage de 5 mn au bain-marie bouillant.

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Mass spectrometry of volatile mercury salts

(*Received* 2 *August* 1968. *Accepted* 24 *September* 1968)

IN A STUDY of the mercury photosensitization of alkyl halides it became of interest to determine the amount of mercury(II) chloride produced. The total quantity arising from the interaction of mercury vapour and the alkyl halide at room temperature in a photolysis cell of 50 ml capacity was a few μg. Much smaller amounts than this of volatile metal chelates have been measured by the integrated ion current method[1-3] and the conversion of the mercury(II) chloride into such a chelate was at first envisaged. For application of this technique the compound concerned should have a very low vapour pressure at room temperature but evaporate rapidly at temperatures between 200 and 500°. Mercury(II) chloride satisfies this requirement, so there is no need to convert it into a chelate. This paper describes the use of the technique to determine μg quantities of mercury chloride.

EXPERIMENTAL

Mercury(I) and (II) chlorides were obtained as analytical grade reagents, and a 0·1% solution of mercury(II) chloride was made in pure ethanol. All measurements were made with a G.E.C.–A.E.I. MS 9 mass spectrometer.

Method

The principle has been described previously.[1] Volumes of ~1 μl of mercury(II) chloride solution were injected into the sample holder of the direct insertion probe by means of a Hamilton syringes The probe was then transferred to the vacuum system of the mass spectrometer and held at room temperature. With the aid of the standard mass marker (heptacosafluorotri-n-butylamine) and the peak-matching facilities of the instrument, it was tuned to an *m/e* value of 268. The probe was then lowered into the ion source which was held at a temperature of 250°. The evaporation of the sample of mercury(II) chloride could be followed by watching the rise and fall of the *m/e* 268 peak on the oscilloscope. At the same time, the ion current at this *m/e* value was recorded. It was found convenient to cut off the supply of the reference compound during this recording. The area under the recorder trace was proportional to the integrated ion current and was measured. A calibration graph of peak area against weight of mercury(II) chloride was constructed.

RESULTS AND DISCUSSION

The boiling point of mercury(II) chloride is given as 302°.[4] It therefore appeared possible that its vapour pressure would be sufficiently low at room temperature for no detectable evaporation to occur under the high vacuum conditions in the source of the spectrometer. Further, since the salt vapourizes without substantial decomposition at elevated temperatures the mass spectrum was expected to contain a peak, corresponding to the molecule ion, sufficiently intense to permit use of the integrated ion current technique. The appreciable vapourization that took place at room temperature was entirely unexpected. The mass spectrum recorded during this evaporation at room temperature was surprisingly complex, but no ions corresponding to $HgCl_2^+$ could be detected. Because of the isotopic constitution of mercury, all ions containing mercury gave at least six peaks in the spectrum. Precise mass analysis of one peak from each group showed that the mass spectrum was due to ions from the molecular species HgI_2 and $HgBr_2$. There was also a peak corresponding to HgBrI which might exist independently or be formed during the evaporation. The boiling points for the bromide and iodide, 322° and 354°, are both higher than that of the chloride, so their vapour pressure–temperature curves must be less steep, reflecting their covalent nature. When the sample of mercury(II) chloride was lowered into the heating region of the ion source, held at 250°, peaks appeared in the mass spectrum corresponding to the ions $HgCl^+$, $HgCl_2^+$ and $HgBrCl^+$. The concentration of other mercury(II) halides in the chloride is not quoted in the specification, and it is unfortunate that the present technique cannot be used to assess their amounts, because of their greater volatility. It is certain, however, that they are minor constituents and their detection is only made possible by their preferential evaporation into the ion source.

A sample of mercury(I) chloride slurried in alcohol was admitted to the mass spectrometer in the same way, and also gave a spectrum characteristic of the higher mercury halides.

The peak used for measurement was at *m/e* 268, corresponding to the species $^{198}Hg^{35}Cl_2^+$. When approximately 1 μg of mercury(II) chloride was evaporated, the ion current peak obtained at *m/e* 268 was quite sharp, and the calibration curve was linear; from the slope of the curve the sensitivity s_{268} was calculated as 27·5 mm^2/μg. This sensitivity is obtained at low instrumental gain in order to facilitate calibration. Very much higher sensitivities are possible with increased electron multiplier gain. The sensitivity compared with that for some metal chelates is low but this is due partly to the fact that the mass peak at *m/e* 268 is produced by only 6% of the total molecule ion current.

Acknowledgement—The author is indebted to Miss M. J. A. Reade for carrying out mass spectrometric analyses.

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Summary—The integrated ion current method is applied to the determination of μg quantities of mercury(II) chloride. The mass spectra of both mercury(I) and (II) chlorides indicate that the analytical reagent grade chemicals contain traces of mercury(II) bromide and iodide.

Zusammenfassung—Die Methode des integrierten Ionenstroms wird auf die Bestimmung von μg-Mengen Quecksilber(II)-chlorid angewandt. Die Massenspektren von Quecksilber(I)- und -(II)-chlorid zeigen daß auch die Reagentien "zur Analyse" Spuren von Quecksilber(II)-bromid und -jodid enthalten.

Résumé—On applique la méthode du courant d'ions intégré au dosage de quantités de chlorure de mercure(II) de l'ordre du μg. Les spectres de masse des deux chlorures de mercure(I) et (II) indiquent que les produits de qualité réactif analytique contiennent des traces de bromure et iodure de mercure(II).

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Improved selectivity of chemical colour reactions by simple gas chromatographic separation

(*Received* 20 *May* 1968. *Accepted* 28 *September* 1968)

THE use of chemical spot tests in the identification of gas chromatograph effluents has been described by Dubois and Monkman.[1] Two examples are given below in which a simple chromatographic separation is used on a column designed to remove specific interfering agents in sensitive chemical tests; no complex apparatus is required.

EXPERIMENTAL

Detection of traces of formaldehyde in the atmosphere

The Dräger Gas Detector consists essentially of a hand-operated pump into which is fitted a tube containing a solid absorbent suitably impregnated with a reagent (aromatic hydrocarbon–sulphuric acid in the tubes for formaldehyde testing) which changes colour in contact with the contaminant sought.

The pump is operated five times to draw a set volume of air through the reagent tube, and the concentration of formaldehyde is indicated by the length of the red stain in the calibrated tube.

When the detector is used for the determination of ~5 ppm of formaldehyde in the presence of excess of styrene an interfering yellow colour is obtained; *o*- and *p*-cresol vapours reduce the intensity of the red stain. A short tube containing 30% of polyethylene glycol 400 on Embacel (May and Baker Ltd.) was attached to the reagent tube. This column packing was prepared in the normal way by slurrying the polyethylene glycol and Embacel in methylene chloride, evaporating the solvent with gentle mixing to maintain even distribution, and finally oven-drying at 100° for 16 hr.

The tubes (110 ± 2 mm × 6 ± 0·25 mm i.d.) were packed by vibration and tapping and plugged with glass wool at each end before storage in a desiccator until required for use. Each tube contained 0·6 g of packing and was discarded after each test.

When this column was used no interference was found from styrene or from *o*- or *p*-cresol, as shown by the results in Table I.

TABLE I

	Formaldehyde concentration, *mg/m*^{3}		
		Found	
Interfering compound	Added	Without column	With column
Styrene	20	20 yellow-brown stain	20
	5	20	5
o-Cresol	20	5	20
	5	2 very faint colour	5
p-Cresol	20	5	20
	5	negligible colour	4

Detection of acetaldehyde

The acetaldehyde formed by pyrolysis of a mixture of calcium acetate and formate is detected in the gas phase by means of the nitroprusside colour reaction.[2] This test was used for detection of traces of acetate, but phenols liberated from associated materials cause interference with the colour.

A slow stream of nitrogen was passed through the reaction vessel to sweep the pyrolysis products through a glass column (70 mm × 9 mm o.d.) containing 15% polyethylene glycol 400 on Embacel, and then on to a filter paper impregnated with the colour reagent. The interference was again eliminated but the column could be used for a number of determinations before being discarded.

Discussion

In both cases the chemical removal of interfering substances would be extremely difficult owing to the highly reactive nature of formaldehyde and acetaldehyde, whereas the separation by gas chromatography is simple. The wide range of selective stationary phases available may allow simple separations of this type to be widely applied to the removal of specific substances causing interference in organic chemical spot tests.

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Summary—Gas chromatography is applied to improve the selectivity of sensitive organic colour tests without the use of complicated apparatus.

Zusammenfassung—Zur Verbesserung der Selektivität empfindlicher organischer Farbtests ohne Verwendung komplizierter Geräte wird die Gaschromatographie angewandt.

Résumé—On a appliqué la chromatographie en phase gazeuse pour améliorer la sélectivité d'essais colorés organiques sensibles sans l'emploi d'appareil compliqué.

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Arsenazo III and its analogues—VI*

Some new photometric reagents for palladium

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A SERIES of mono and bisazo compounds have been proposed as reagents for palladium: pyridylazoresorcinol (ε 18·4 × 10^3),[1,2] arsenazo III (ε 16 × 10^3)[3,4] and 2,7-bis(4-arsonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid (ε 28 × 10^3).[5] The last two belong to the class of 2,7-bisazo derivatives of chromotropic acid.[6] We have now studied the colour reaction of palladium with 12 reagents of this class. These compounds had already been studied as reagents for actinides (U, Th, Pu, Pa, Np),[6–8] for Zr, Hf, Nb, Sc, for lanthanides,[6,9–11] and for Ba, Sr, S, Al, Ga, In, Mo.[6,12]

The reagents were synthesized, purified and analysed according to a scheme already published.[6] An excess of the diazonium salt of the corresponding amine was added to a concentrated solution of

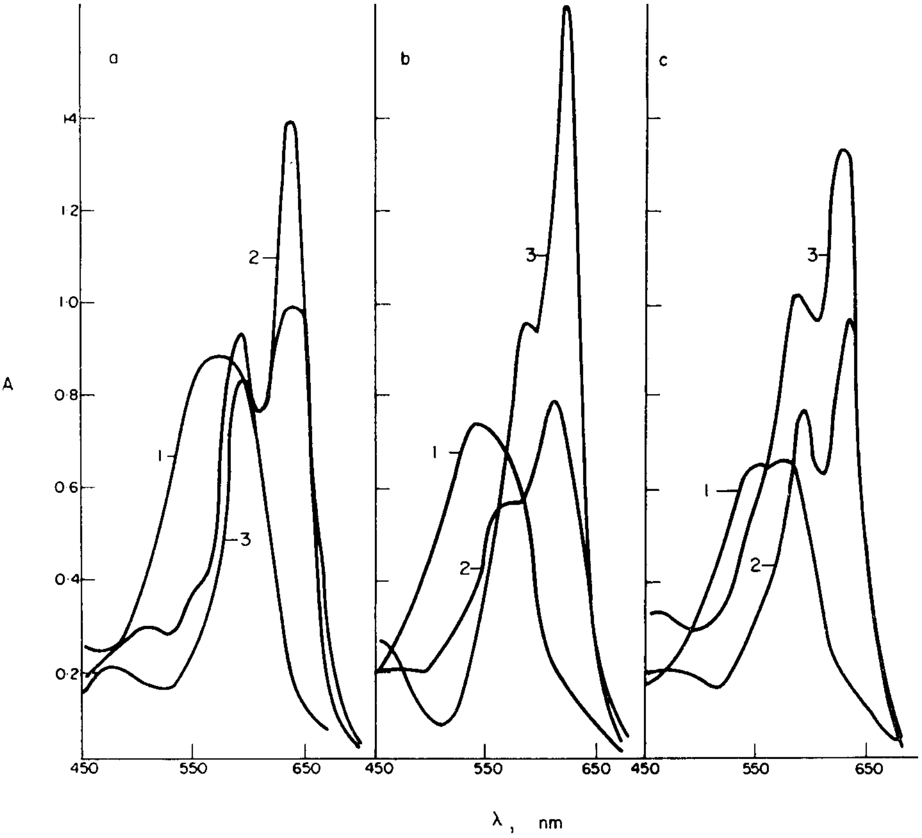


FIG. 1.—Absorption spectra of reagents 3, 6 and 8 and their Pd complexes at pH 3.
(*a*) Reagent 3: *1*—[R] = 2 × $10^{-5}M$; *2*—[R] = 2 × $10^{-5}M$; [Pd] = 8 × $10^{-5}M$; *3*—[R] = 8 × $10^{-5}M$; [Pd] = 2 × 10^{-5}[M].
(*b*) Reagent 6: *1*—[R] = 1·4 × $10^{-5}M$; *2*—[R] = 1·4 × $10^{-5}M$; [Pd] = 5·6 × $10^{-4}M$; *3*—[R] = 8 × $10^{-5}M$; [Pd] = 2 × $10^{-5}M$.
(*c*) Reagent 8: *1*—[R] = 1·6 × $10^{-5}M$; *2*—[R] = 1·6 × $10^{-5}M$; [Pd] = 6·4 × $10^{-5}M$; *3*—[R] = 8 × $10^{-5}M$; [Pd] = 2 × $10^{-5}M$.
For curves *1* and *2*, reference was water, for curve *3*, 6 × $10^{-5}M$ reagent.

chromotropic acid or a monoazo compound in a mixture of potassium hydroxide, calcium hydroxide and lithium chloride[13] and the reaction mixture was acidified with conc. hydrochloric acid. The product was purified by repeated recrystalilzation from water or aqueous ethanol. Its purity was established by paper chromatography with a 20% solution of calcium chloride in 1*M* hydrochloric acid. The products were analysed for As, N and S, and assayed by potentiometric and spectrophotometric titrations.[14]

The colour reactions with palladium in hydrochloric, perchloric and sulphuric acid media were studied. Typical absorption spectra are shown in Fig. 1. The reagents are crimson and palladium forms blue or blue-green complexes. The influence of acidity and the nature of the acid is shown in Fig. 2 for reagent 8; the others behave similarly. The nature of the acid is extremely important.

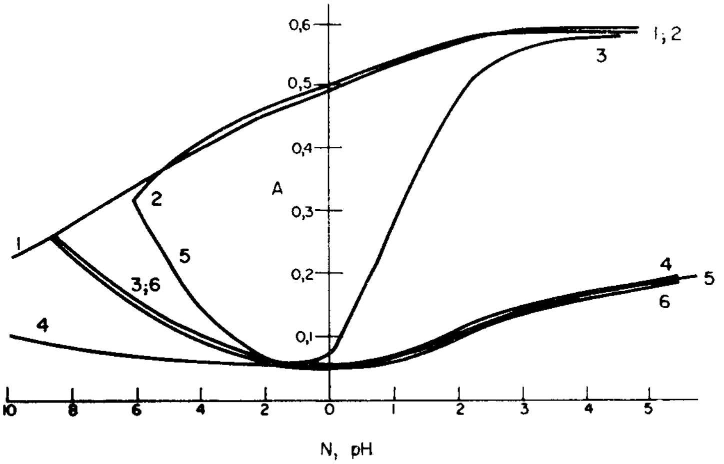


FIG. 2.—Effect of nature and acidity of the solution on the absorbance of reagent 8 and its palladium complex.
1, *2*, *3*—complex in H_2SO_4, $HClO_4$, HCl media respectively
4, *5*, *6*—reagent in H_2SO_4, $HClO_4$, HCl media respectively.
[R] = [Pd] = $8 \times 10^{-6}M$; $\lambda = 620$ nm.

In sulphuric or perchloric acid the optimum acidity is between pH 5 and 2*N* acid, whereas with hydrochloric acid it is between pH 2·5 and 5 (because of formation of chlorocomplexes of palladium). Addition of sodium chloride lowers the absorbance. Outside the acidity range between pH 5 and 2*N* acid, the difference in absorption by reagent and complex is reduced on account of a deepening of the colour of the reagent, but the molar absorptivity of the complex is high enough (60–80 × 10^3) in 3–5*N* sulphuric acid for a higher acidity to be used; at the same time the selectivity is increased.

High concentrations of salts slow the development of the colour (Fig. 3). For full development, sulphuric acid solutions (from 5*N* to pH 1) should be heated for 20 min at 80°; solutions at pH > 2 need be heated only for 5–7 min at 60°.

The characteristics of the colour reactions are summarized in Table I. It can be seen that the reagents with only one *o*,*o*′-dihydroxyazo grouping (reagents 3, 6–8) are the most sensitive. Many elements react with this class of reagent, but generally do not give a colour reaction in sulphuric acid medium. Table II shows the effect of various cations on the reaction of palladium with reagent 6—Sulphonitrophenol M—in 3*N* sulphuric acid, and illustrates the high selectivity.

The composition of the complexes was established by the mole ratio method (Fig. 4). The reagents may be split into two groups—the monofunctional with only one salt-forming group *ortho* to the azo group (2, 5–7, 10, 11)—and the bifunctional with two such groups. The absorption spectra differ according to which component is in excess in the solution, indicating the existence of more than one complex. The break-points at mole ratios of Pd:R = 1:1 and 2:1 are shown in Fig. 4. Previously, Me_2R complexes were known only for copper(II) and vanadium(IV)[14] with bifunctional reagents of the arsenazo III group. From spectrophotometric and potentiometric investigations the conclusion was reached that the *o*-hydroxy, *o*-carboxy, *o*-arsono-*o*′-hydroxyazo grouping is the one involved in bonding. When two such groups are present, 1:1 complexes form with excess of reagent,

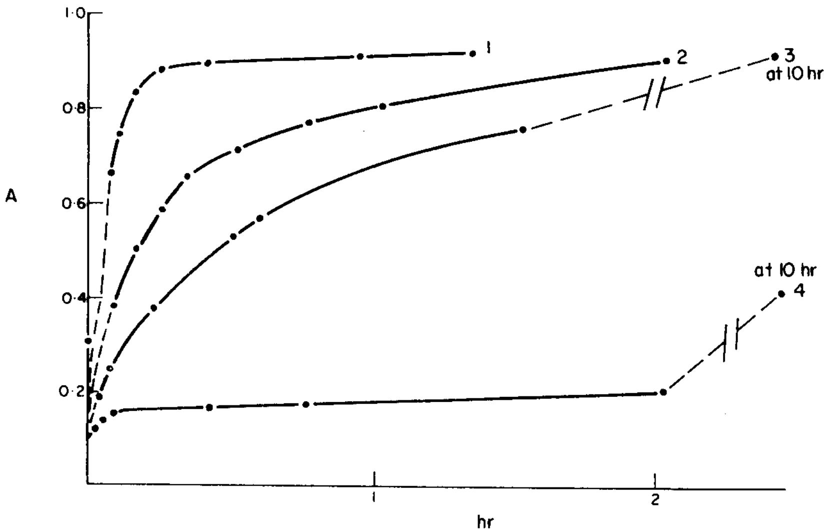


FIG. 3.—Influence of anion concentration on development time for Pd complex of reagent 8.
1—pH 3·5; *2*—pH 1·1 (H_2SO_4); *3*—1*N* H_2SO_4;
4—pH 1·1 (H_2SO_4 + 0·2*M* NaCl).
[R] = [Pd] = 1·6 × 10^{-5}*M*; λ = 620 nm.

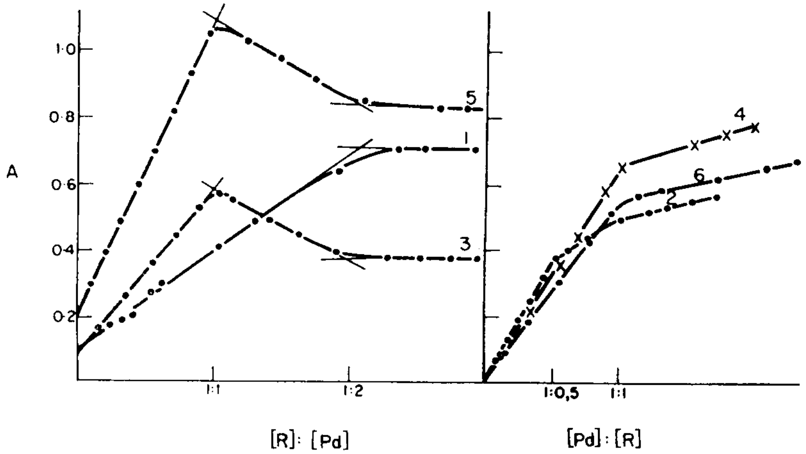


FIG. 4.—Determination of composition of the Pd complexes of reagents 3 (curves *1* and *2*), 6 (curves *3* and *4*) and 8 (curves *5* and *6*) at pH 3.
1—[R] = 1 × 10^{-5}*M*; *2*—[Pd] = 1 × 10^{-5}*M*;
3—[R] = 6·8 × 10^{-6}*M*; *4*—[Pd] = 4 × 10^{-6}*M*;
4—[R] = 1·6 × 10^{-5}*M*; *6*—[Pd] = 8 × 10^{-6}*M*.
1, *2*—λ = 630 nm; *3*–*6*—λ = 620 nm.
Reference water.

TABLE I.—COLOUR REACTIONS OF PALLADIUM AT pH 3

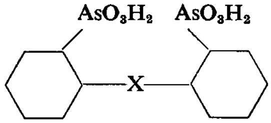
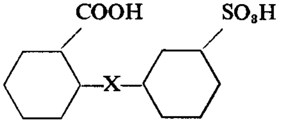
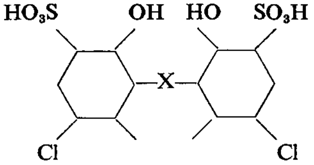
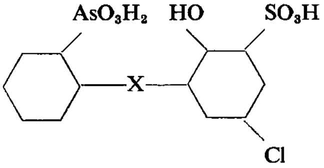
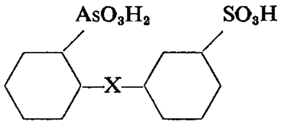
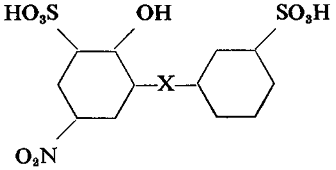
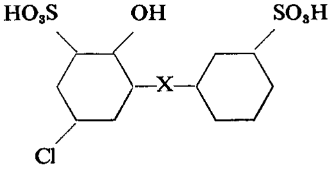
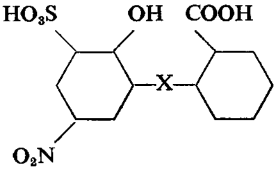
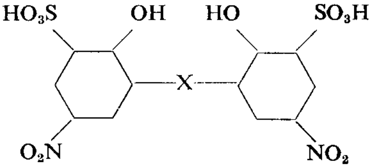
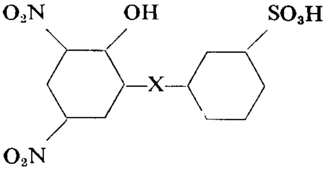
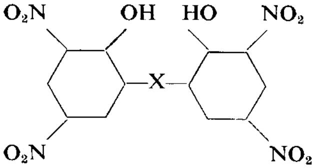
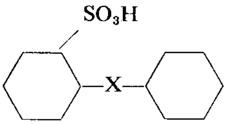
			Complex			
		Reagent	With excess of Pd		With excess of reagent	
	Reagent	λ_{max}, *nm*	λ_{max}, *nm*	ε	λ_{max}, *nm*	ε
1.		540	620	33,000	600	20,000
2.		540	610	31,500	580 620	50,000
3.		560	590 640	70,000	590 640	50,000
4.		560	590 630	55,000	590 630	40,000
5.		540	620	30,000	620	28,000
6.		540	570 610	55,000	580 620	82,000
7.		550	620	40,000	590 620	60,000
8.		550 570	590 630	61,000	580 620	70,000

Table 1 (continued)

	Reagent	Reagent	Complex: With excess of Pd		Complex: With excess of reagent	
		λ_{max}, *nm*	λ_{max}, *nm*	ε	λ_{max}, *nm*	ε
9.		550	580 630	52,000	580 630	52,000
10.		550	600	40,000	530 630	38,000
11.		550	620 670	50,000	very feeble reaction	
12.		540	625	30,000	645	14,000

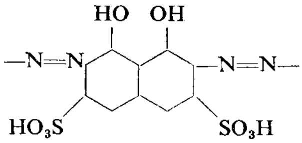
X = 

TABLE II.—INTERFERENCES IN PALLADIUM DETERMINATION WITH SULPHONITROPHENOL M IN $3M$ SULPHURIC ACID

Cation	Amount added to 20 μg of Pd, *mg*	Absorbance at 620 nm	Relative error, %	Cation	Amount added to 20 μg of Pd, *mg*	Absorbance at at 620 nm	Relative error, %
—	—	0·710	—	Cu	0·3	0·710	0
Fe	2·5	0·705	−0·5				
	6·0	0·710	0		0·6	0·720	+1·5
	10·0	0·650	−8·5		1·5	0·750	+5·5
Co	3·5	0·710	0	VO^{2+}	2	0·730	+3·0
	6·5	0·720	+1·5		4	0·725	+2·0
	13	0·770	+8·5		8	0·760	+7·0
Ni	10	0·730	+3·0	Zr	0·04	0·720	+1·5
	20	0·740	+4·0		0·08	0·730	+3·0
	50	0·800	+11·5		0·2	0·760	+7·0
Al	5	0·710	0	Mo	0·1	0·710	0
	10	0·690	−2·5		0·3	0·710	0
	20	0·600	−15·5		0·5	0·750	±5·5

Table 2 (continued)

Cation	Amount added to 20 μg of Pd, *mg*	Absorbance at 620 nm	Relative error %	Cation	Amount added to 20 μg of Pd, *mg*	Absorbance at 620 nm	Relative error, %
	5	0·710	0		0·2	0·710	0
Ga	10	0·700	−1·5	Sc	0·3	0·710	0
	15	0·640	−10·0		0·6	0·730	+3·0
	10	0·730	+3·0		0·01	0·745	+5·0
In	15	0·710	0	Nb	0·02	0·765	+7·5
	20	0·730	+3·0		0·04	0·830	+11·5
	3	0·710	0		0·2	0·710	0
Ca	6	0·730	+3·0	Rh	1	0·705	−0·5
	12	0·755	+6·0		2	0·710	0
Mg	15	0·700	−1·5		0·2	0·700	−1·5
	20	0·705	−0·5	Pt	1	0·710	0
	0·2	0·710	0		2	0·705	−0·5
Ba	Precipitation with larger amounts of Ba						
	10	0·715	+0·5				
La	15	0·710	0				
	20	0·760	+7·0				

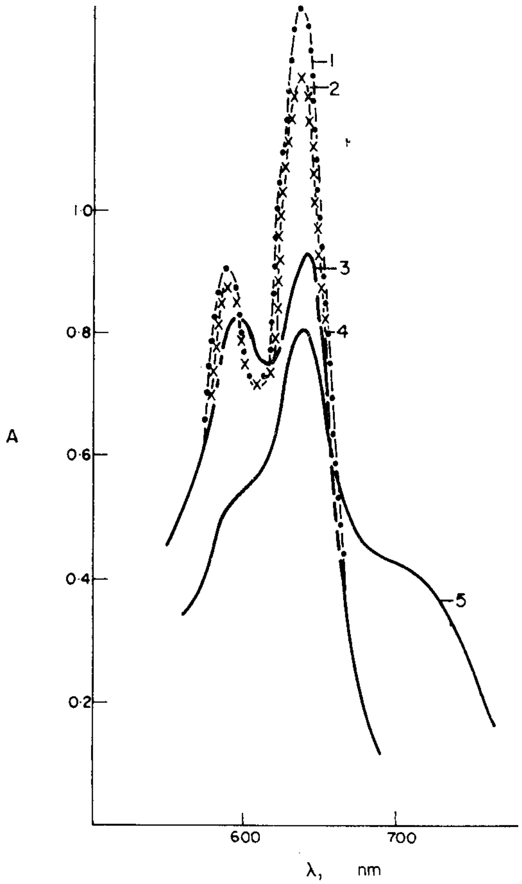


Fig. 5.—Absorption spectra of Sulphochlorophenol S (reagent 3) with Pd. *1*, *2*—[R]: [Pd] = 1:2, pH 3 and 12 respectively; *3*, *4*—[R]: [Pd] = 1:1, pH 3 and 7 respectively; *5*—[R]: [Pd] = 1:1, pH 9·2.

and 2:1 Me:R complexes with excess of metal ion.[14] The mechanism for palladium seems to be similar. Figure 5 shows the absorption spectra of Sulphochlorophenol S with palladium at 1:1 and 2:1 ratios of metal to reagent, at various pH values. The position of λ_{max} for the 2:1 complex does not change over a wide pH range (3–12). This makes it reasonable to suppose that all the groups of the reagent participate and that ionization of the four hydroxy groups is responsible for the colour change.[14] In the case of the 1:1 complex, the colour over the pH range up to 7·5 may be attributed to participation in complex formation by the hydroxy group of the first benzene ring. The deepening in colour at pH > 7·5 is caused by dissociation of the hydroxy group in the second benzene ring, which is not involved in complex formation.

The results for the monofunctional reagents make it likely that with an excess of reagent the complexes will be 1:1. At the same time, the mechanism of complex formation does not seem to differ from that for palladium [and copper(II) or vanadium(IV)] with the bifunctional reagents. In the 2:1 complexes, however, the *peri*dihydroxy grouping of chromotropic acid or the second *o*′-hydroxyazo grouping may be the one involved in complex formation.

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Summary—Colour reactions of palladium with 2,7-bisazo derivatives of chromotropic acid, containing the *o,o*′-dihydroxyazo group, are characterized by high sensitivity ($\varepsilon = 60–82 \times 10^3$) and good contrast ($\Delta\lambda = 70–80$ nm) and permit determination of palladium over a wide range of acidity (from pH 5 to 4*N* sulphuric acid). Many other metals, including the other platinum metals, do not interfere when present in up to 100-fold amounts.

Zusammenfassung—Farbreaktionen von Palladium mit 2,7-Bisazoderivaten der Chromotropsäure, die die *o,o*′-Dihydroxyazogruppe enthalten, sind charakterisiert durch hohe Empfindlichkeit ($\varepsilon = 60–82 \cdot 10^3$) und guten Kontrast ($\Delta\lambda = 70–80$ nm). Sie erlauben die Bestimmung von Palladium in einem weiten Aciditätsbereich (von pH 5 bis 4N Schwefelsäure). Viele andere Metalle, darunter die anderen Platinmetalle, stören in bis zu 100-facher Menge nicht.

Résumé—Les réactions colorées du palladium avec des dérivés 2,7-bisazo de l'acide chromotropique, contenant le groupement *o,o*′-dihydroxyazo, sont caractérisés par une sensibilité élevée ($\varepsilon = 60–82 \times 10^3$) et un bon contraste ($\Delta\lambda = 70–80$ nm) et permettent la détermination du palladium dans un large domaine d'acidité (de pH 5 à l'acide sulfurique 4 *N*). De nombreux autres métaux, y compris les autres métaux de la famille du platine, n'interfèrent pas lorsqu'il sont présents jusqu'à des quantités 100 fois supérieures.

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Determination of caesium-137 in fast-reactor coolant systems

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In fast-reactor systems employing vented fuel cans, fission products may escape into the liquid metal coolant (sodium–potassium). Caesium-137 is liberated in nuclear reactors as a fission product and it is of great importance to know the concentration of it in the coolant. Owing to its long half-life (30 y) its activity falls only slightly during the initial cooling period.

It is well known that salts of inorganic polyacids are suitable ion-exchangers and that, in particular, ammonium molybdophosphate (A.M.P.) shows considerable selectivity for caesium.[1] It is not surprising therefore that the use of this reagent for the determination of trace amounts of caesium-137 has been reported by a number of workers.[2,3] However, both the papers cited and those of other workers have been concerned solely with the separation and recovery of caesium-137 from solutions of mixed fission products.

In the estimation of caesium-137 in fast-reactor coolants the problem is exceptional in that other alkali metals are present in extremely large excess and are likely therefore to interfere with the determination. The object of this work was to investigate the conditions under which the A.M.P. reagent might be used.

EXPERIMENTAL

Ammonium 12-*molybdophosphate*

A.M.P. was prepared by mixing a solution of 6 mg of phosphate ion (as ammonium dihydrogen orthophosphate) in 16 ml of 2*M* nitric acid with 6 ml of 10% ammonium molybdate solution. The mixture was heated at 80° for 20 min and gave a yield of 120 mg of A.M.P. This precipitate was washed into a sintered glass crucible (20-mm diameter, porosity 4) and gave a suitably thick and even layer for the exchange process.

Counting procedure

All radioactive samples were counted with a well-type NaI(Tl) scintillation counter and associated electronic equipment. The scintillator crystal held a 15-mm diameter glass sample bottle. The same volume (6 ml) of solution was used throughout, giving constant geometry for all samples. The optimum photomultiplier tube voltage and discriminator voltage were determined in the usual way, 6 ml of a standard caesium-137 solution being used. This standard solution was counted each day and corrections made for any variation shown.

The standard caesium-137 solutions were made by diluting a stock solution of caesium so that a count of 2–6 × 10^4 cpm/ml was obtained. Nitric acid (1*M*) was used to make up the solution and 1 mg of caesium chloride/250 ml was added to act as a carrier.

Exchange process

Two series of experiments were performed, the first with 6-ml portions of caesium-137 solution in varying nitric acid concentrations and the second with 6-ml portions of the caesium-137 solution containing differing amounts of sodium and potassium. These solutions were counted and slowly passed through a prepared sample of A.M.P. under slight vacuum at a rate of approximately 30 drops/min. The solution was thoroughly washed through with 50 ml of 1*M* nitric acid. The A.M.P. was then dissolved in 5*M* ammonia, made up to 6 ml with water and recounted. The amounts of sodium and potassium added were fractions of the calculated amount of each which could replace all the ammonium ions in the 120 mg of A.M.P. used.

The exchange process was then applied to 6 ml of a 2*M* nitric acid solution of sodium–potassium reactor coolant (containing a total weight of 12 mg of potassium and sodium) contaminated with fission products which had been allowed to decay for 1 year. The activity of the solution was 2 × 10^5 cpm/ml, composed mainly of 4 × 10^4 cpm ^{95}Zr/^{95}Nb, 2 × 10^4 cpm ^{137}Cs, 2 × 10^4 cpm ^{144}Ce and 10^5 cpm ^{106}Ru. In order to prevent the retention of zirconium and niobium by the A.M.P. two drops of concentrated hydrofluoric acid were added to the 6 ml of test solution, but the spectrum of the A.M.P. solution then clearly showed the presence of cerium-144 as well as caesium-137; to eliminate the cerium, it proved necessary to increase to 250 ml the amount of 1*M* nitric acid used for washing. Confirmation of the presence of only caesium-137 on the A.M.P. was obtained by normal spectrum stripping techniques.

RESULTS AND DISCUSSION

The first series of experiments showed that the caesium-137 was most efficiently extracted from solutions of nitric acid of concentration between 1*M* and 3*M*. At concentrations above 3*M* the efficiency rapidly decreased, probably owing to decomposition of the A.M.P. by the nitric acid. The results obtained were in complete agreement with those already published by Krtil.[4]

The effect of the presence of relatively large quantities of sodium and potassium on the estimation of caesium-137 is shown in Table I. The first column shows the ratio of sodium or potassium ions

TABLE I

Na^+ or K^+ ratio to A.M.P. NH_4^+	Total count of 6 ml of ^{137}Cs solution	Total count of 6 ml of A.M.P. solution	Deviation, %	Relative standard deviation, from counting statistics, %
Na 0·5	282625	282359	−0·09	±0·27
	286168	285943	−0·08	±0·26
0·75	270985	271605	+0·23	±0·27
	275915	275596	−0.12	±0·27
1·0	272949	272230	−0.26	±0.27
	283538	284105	+0·20	±0.27
1·5	274363	273646	−0.26	±0.27
	268925	268548	−0·14	±0·27
2·0	272428	271516	−0·33	±0·27
	285650	285413	−0·08	±0·27
4·0	439996	439168	−0·19	±0·21
	448762	448594	−0·04	±0·21
8·0	387982	388694	+0·18	±0·23
	388728	388488	−0·06	±0·23
16·0	404652	402042	−0·64	±0·22
	385487	383642	−0·48	±0·23
32·0	400994	393296	−1·92	±0·22
	407182	402646	−1·11	±0·22
64·0	401698	398848	−0·71	±0·22
	384225	380385	−1·00	±0·23
128·0	428273	423767	−1·05	±0·22
	386483	378131	−2·16	±0·23
K 0·5	287519	287857	+0·12	±0·26
	280245	279823	−0·15	±0·27
1·0	269618	268828	−0·29	±0·27
	282874	283187	+0·11	±0·27
2·0	281105	280385	−0·26	±0·27
	269320	270104	+0·29	±0·27
4·0	405262	400012	−1·29	±0·22
	408389	400043	−2·04	±0·22
8·0	406567	404563	−1·81	±0·22
	410609	407903	−0·66	±0·22
16·0	406364	393056	−3·20	±0·22
	390871	379537	−2·89	±0·22
32·0	388693	367777	−5·38	±0·22
	406942	368722	−9·39	±0·22
64·0	382820	270530	−29·30	±0·21
	382062	261180	−31·63	±0·21

added, to ammonium ions present in the precipitate. It can be seen that for 100% efficiency sodium up to 16 times or potassium up to twice the amount needed to replace completely all the ammonium ions in the A.M.P. can be tolerated. Because the ionic size of potassium is greater than that of sodium, the former competes more strongly with caesium for the lattice holes in the A.M.P., thus causing loss of caesium extraction efficiency at a lower concentration.

If an extraction efficiency of 98% is acceptable then the analytical procedure described above will work with 128 times as much sodium or 16 times as much potassium as that required to replace completely the ammonium of the A.M.P. In the case of sodium in the form of nitrate or chloride this is approximately a saturated solution.

When applying the method to a solution of alkali metal reactor coolant contaminated with fission products, it is necessary to increase the amount of $1M$ nitric acid, as already indicated, to prevent retention of cerium-144 on the A.M.P.

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Summary—A method for the separation of caesium by ion-exchange involving ammonium 12-molybdophosphate has been investigated, and found to be 100% efficient for aqueous solutions with high sodium and potassium concentrations.

Zusammenfassung—Ein Verfahren zur Abtrennung von Caesium durch Ionenaustausch mit Ammonium-12-molybdophosphat wurde untersucht. Sein Wirkungsgrad ist in wäßrigen Losungen mit hohen Natrium- und Kaliumkonzentrationen 100%.

Résumé—On a étudié une méthode pour la séparation du caesium par échange d'ions mettant en jeu le 12-molybdophosphate d'ammonium et on l'a trouvée efficace à 100% pour les solutions aqueuses à hautes concentrations en sodium et potassium.

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Potassium thiocarbonate as a complexing agent and precipitant

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THE qualitative[1-3] and quantitative[4,5] analytical applications of potassium thiocarbonate (PTC) have been extensively studied. The use of precipitation from homogeneous solution in conjunction with PTC offers numerous possibilities for the analytical separation of metal ions. PTC, besides serving as an efficient source of sulphide and thiocarbonate ions in solution for the precipitation of cations, is also capable of producing soluble complex thiocarbonates of certain metals, and so can serve simultaneously as precipitant and masking agent. Most of the complexes are intensely coloured and some permit spectrophotometric estimation. This communication describes titrimetric and gravimetric procedures for milligram quantities of Mo(VI), Tl(I), Se(IV), Te(IV) and V(V).

EXPERIMENTAL

Reagent

Potassium thiocarbonate, $1M$. Prepared and standardized as reported earlier.[6,7]

Determination of molybdenum(VI)

Gagliardi and Pilz[8] used sodium thiocarbonate to precipitate molybdenum sulphide. With molybdenum(VI) PTC forms a soluble complex which is stable in alkaline molybdenum but gives molybdenum sulphide on acidification. Silver, lead, bismuth and cadmium are precipitated as their thiocarbonates in ammoniacal medium; titanium, zirconium and thorium are precipitated as hydroxides. Molybdenum can also be separated from titanium, zirconium, thorium, iron(III), nickel and zinc by precipitation with PTC at pH 0·5–0·7.

Procedure. To 100 ml of an aqueous solution of molybdate (corresponding to $\ngtr 50$ mg of molybdenum trioxide) add aqueous 1*M* PTC solution until the solution is dark red owing to the formation of the thiocarbonatomolybdenum complex. Filter off any precipitate (silver, *etc*) and gradually acidify the filtrate with 3*M* sulphuric acid to precipitate the sulphide. Add enough acid to make the solution about 0·5*M* in sulphuric acid. Digest the precipitate on a steam-bath for 30 min, cool, and collect it by filtration (Whatman No. 42 paper). Wash the precipitate thoroughly with water, dry and ignite it[9] at 460–780° to the oxide. Alternatively, add PTC direct to an acid solution containing molybdenum.

Determination of thallium(I)

The ease with which thallium(I) thiocarbonate is precipitated in a highly dense and pure form affords an efficient method for standardizing PTC solutions.[8]

Interfering anions are iodide, chromate and others which give insoluble thallium(I) salts. The interfering cations have thiocarbonates, sulphides or hydroxides which are precipitated on addition of PTC. Silver, mercury(II), copper(II), iron(III), cobalt(II) and nickel can be masked by addition of potassium cyanide to a solution made slightly ammoniacal. Aluminium, chromium(III), beryllium and titanium can be masked with tartaric acid. PTC itself can act as masking agent for copper(II), iron(III), cobalt(II), nickel, arsenic(III, V), antimony(III, V) and molybdenum(VI). For complete formation of the iron(III) complex the solution must be warmed, and acetate interferes in the masking. Cobalt and iron are co-precipitated if present in more than equimolar amount relative to thallium(I), but this can be prevented by adding tartrate or EDTA as masking agents. EDTA efficiently masks iron(III), cobalt(II), nickel, zinc, barium, calcium, strontium and magnesium in alkaline medium.

The thiocarbonate complex of copper(II) is more stable than the copper-EDTA complex, so is preferentially formed but is stable enough not to interfere.

Procedure. Add an appropriate masking agent to an aliquot of an aqueous solution containing $\sim$1 mg of Tl(I) per ml, then add 0·1*M* PTC dropwise with stirring till the vermilion precipitate settles down and the supernatant liquid is yellow with excess of reagent. Filter off the precipitate on a porosity 4 sintered-glass crucible, wash with water, dry at 100–110° and weight as Tl_2CS_3. Alternatively, decompose the product with conc. hydrochloric acid and titrate with potassium iodate solution by the Andrews method.

Determination of selenium(IV), tellurium(IV) and vanadium(V)

PTC, when used in excess, forms the thiocarbonato complexes, which on acidification yield the sulphides of these species. Interfering ions can be dealt with as in the case of molybdenum.

Procedure. To an aliquot of solution of the ion to be determined (0·3 mg of the element per ml) add 0·5*M* PTC dropwise with constant stirring till the soluble coloured thiocarbonate complex is obtained. Filter off any precipitate and acidify the filtrate with 1·5–2·0*M* hydrochloric acid and digest on the steam-bath for about 30 min. (Do not digest for vanadium determination.) Cool, and collect on a porosity 4 sintered-glass crucible (selenium and tellurium) or on paper (vanadium). Wash thoroughly with water and finally with alcohol, and dry[10] the selenium sulphide at below 200° and tellurium sulphide at below 180°. Ignite vanadium sulphide to the oxide at above 300°. Alternatively, dissolve the vanadium sulphide in 6*M* sulphuric acid and titrate the vanadium(V) with iron(II) ammonium sulphate solution, with ferroin as indicator.

RESULTS

Analysis of binary mixtures of molybdenum(VI), thallium(I), selenium(IV), tellurium(IV) or vanadium(V) with an interfering cation from those mentioned, gave results of acceptable accuracy, the largest relative error being 1·5% and the average relative error 0·2%.

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Summary—Efficient analytical separations of Mo(VI), Tl(I), Se(IV), Te(IV) and V(V) from various ions have been made possible by using potassium thiocarbonate (PTC) as a complexing and precipitating agent. For gravimetric estimations, thermogravimetric studies of the products have been used to determine the optimum temperature range of ignition.

Zusammenfassung—Mo(VI), Tl(I), Se(IV), Te(IV) und V(V) lassen sich mit Kaliumthiocarbonat als Komplexbildungsund Fällungsmittel in guter Ausbeute von verschiedenen Ionen abtrennen. Bei gravimetrischen Bestimmungen wurden mit Hilfe thermogravimetrischer Untersuchungen der Produkte die optimalen Verglühtemperaturen ermittelt.

Résumé—On a rendu possibles des séparations analytiques efficaces de Mo(VI), Tl(I), Se(IV), Te(IV) et V(V) de divers ions par l'emploi de thiocarbonate de potassium (PTC) comme agent de complexation et de précipitation. Pour les dosages gravimétriques, on a utilisé les études thermogravimétriques des produits pour déterminer le domaine de température optimal de calcination.

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A simple sensitive recording differential refractometer for column chromatography

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DESPITE the very great success enjoyed by the technique of gas chromatography, there are still many separations, particularly those of biological materials of high molecular weight, which are more easily examined by column chromatography on such materials as modified celluloses, ion-exchange resins *etc*. The effluents from such columns are normally monitored by the use of fraction collectors and batchwise testing with suitable reagents. There is a need for a detector which would indicate the presence of the small concentrations of sample material in the effluent in a manner analogous to that of the detectors used in gas chromatography. For effluents of low absorbance, the technique of differential refractometry would appear to be theoretically ideal. However, it suffers from several disadvantages, not the least being the lack of an inexpensive robust recording instrument. Such a device has been constructed and is described below.

There have been many designs of differential refractometers but most exhibit the common feature of accommodating the sample liquid in a hollow prism surrounded by the reference liquid. This is the most sensitive arrangement and a further increase in the movement of the refracted image for a given change in the refractive index can only be achieved by multiplying the number of passages that the beam makes through the cell or by increasing the length of the optical lever. In the interests of compactness and simplicity, multiple reflecting assemblies and long source-to-image distances are to be avoided. It is therefore necessary to use a detector capable of revealing very small displacements of the image, which may be of the order of a fraction of a μm. One of the commonest solutions to these difficulties is to use a pair of matched vacuum photocells connected in opposition, or a single split-cathode photocell, as the detector.[1] The use of such devices requires considerable care in order to reduce noise and to obtain adequate signals which may be recorded for small image displacements.

Recently, a semiconductor device was described by Wallmark,[2] and also by Baker,[3] which is capable of detecting the movement of a spot of light across its surface. This device may be made by alloying an indium pellet onto the back of the n-type germanium wafer in a conventional phototransistor. When the front surface of the wafer is unevenly illuminated, a voltage is developed across the face and this may be measured by means of a pair of ohmic contacts. The device is used in a simple bridge circuit and, provided that the total illumination is sufficiently intense, it is capable of giving electrical signals for image displacements of considerably less that a μm. (Devices of this type were supplied originally by Baker of S.I.R.A., but are now available commerically from Messrs. Hilger and Watts, Ltd.) It was discovered that if the resistances of the two reference arms were made sufficiently high, then the voltage supplied by this device was sufficient to drive a conventional potentiometer recorder. Since no auxiliary power supplies were required and the photodiode was very stable, with a very high signal-to-noise ratio, it provided the ideal detector for a differential refractometer.

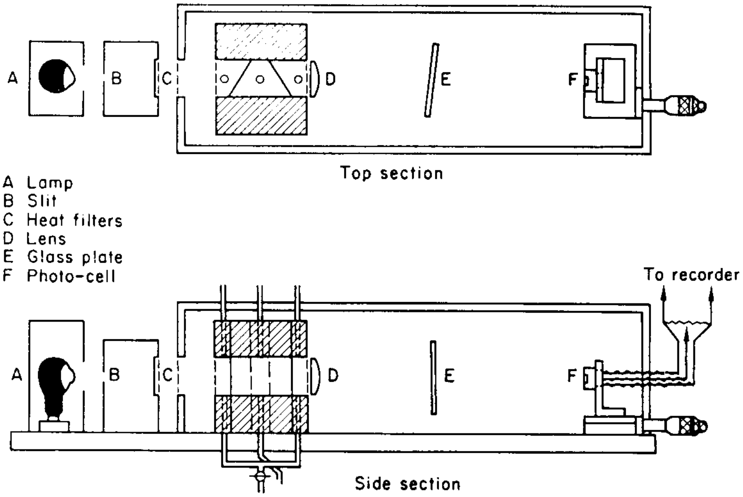

FIG. 1.—Diagram of differential refractometer.

The precision of a differential refractometer used only for the monitoring of column effluents need not be very high and tests of the samples available showed that this detection system had a precision well in excess of the minimum requirements.

Details of construction

In order to obtain the optimum sensitivity with the photodiode, a high level of illumination is required on the sensitive surface. The voltage output from the cell for a standard linear movement of an image smaller in area than the sensitive surface rises to a maximum with increasing illumination, remaining constant above about 0·04 lumen. This requires an intense light-source and as little light as possible must be lost by reflection and multiple refraction. It was finally demonstrated that for a light-source of fixed intensity, the output of the detector for a given displacement was almost independent of the length of the optical lever and the focal length of the imaging lens. The best results were thus obtained by having a very simple optical system in which a vertical slit, width 1 mm, was imaged upon the surface of the photocell by means of a 100-mm focal length planoconvex lens used in the $4f$ position. The slit was illuminated by light from a Phillips 8-V, 50-W lamp. The refractometer cell assembly was interposed between the light source and the lens (Fig. 1). The cell was constructed from a solid block of brass (Fig. 2). A hole, 10 mm in diameter, was drilled along the axis of the block, which was then cut into three pieces by two diagonal cuts, the centre section providing the walls of the hollow prism. After grinding and polishing of the surfaces of the sections to a flat mirror finish, cover slips were placed between the centre section and the two end sections, and also over the external ends of the two outer sections. The outer cover slips were retained by brass end-plates, one of which also carried the lens. The whole assembly was bolted together firmly with six longitudinal bolts and, despite the fact that no jointing material was used, the cell did not leak nor did the cover slips fracture. The massive construction of the cell made it less susceptible to changes in the ambient temperature, and the thin glass membranes separating the three compartments promoted heat transfer between them. The outer two compartments were connected by brass tubing and similar brass tubes allowed access to the compartments from above.

In use, the reference liquid flowed into the top of one outer compartment, through the compartment and out of its base, through the brass connection to the base of the other outer compartment and out of the top. The effluent from the base of the chromatographic column was allowed to flow into the base of the centre compartment and out of the top, whence it was most commonly fed to a fraction collector. The most satisfactory results were obtained when the reference liquid was also the eluting liquid for the column. In this case, the reference liquid passed first through an outer jacket surrounding the chromatographic column, where the temperature became equilibrated. It then passed through the cell and was fed to the top of the column where it acted as the eluent and, after equilibration once again, left the base of the column and entered the centre compartment of the cell.

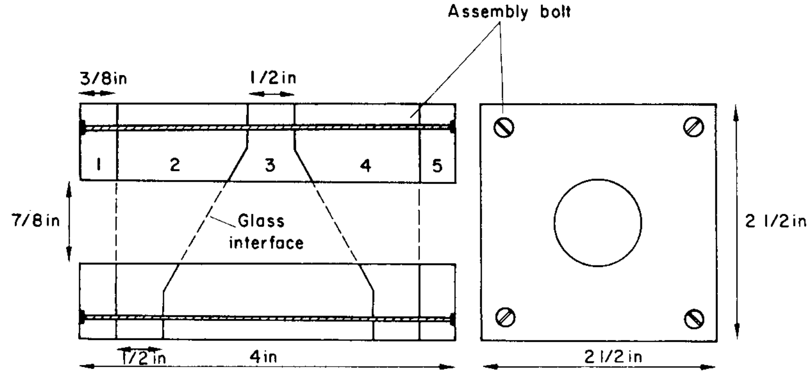

FIG. 2.—The refractometer block.

The greatest source of instability encountered with the instrument was due to changes in ambient temperature, which could cause a temperature differential between the reference liquid and the eluate. To minimize this factor, the column was lagged and the refractometer itself was enclosed in a tight-fitting aluminium box, the walls of which were covered with sheets of expanded polystyrene insulating material. The light-source, which could provide unwanted heat, was kept isolated from the refractometer cell in a separate asbestos lamp-housing and the light was admitted to the cell through heat filters of fused silica.

Since the photodiode could detect very tiny displacements of the image, care was taken to maintain dimensional stability. The whole instrument was mounted on a heavy slate slab, the refractometer cell and the light source being bolted directly to the base. The photodiode itself was mounted on a heavy brass V-slide. The position of the photo-cell could be adjusted by the rotation of a micrometer screw which in turn moved a cam connected directly to the V-slide. With this mechanism, one complete turn of the micrometer screw moved the photo-cell 0·005 in. This adjustment was used to zero the instrument. An alternative method of adjustment which could be used for static measurements was achieved by the rotation, about its vertical axis, of a glass plate interposed between the lens and the detector.

Operation

All the compartments of the sample cell were filled with the eluting liquid and the cell inlets were attached to the base of the column and the eluting feed (or to a separate flow of the same liquid). The lamp was then switched on and the voltage adjusted by means of a Variac transformer to a value below its normal operating voltage so that the lamp operated with reduced brilliance. Since the sensitivity of the detector is proportional to the intensity of illumination, the lamp voltage provided a simple means of attenuation so that the instrument could be set to zero without difficulty. The deflection on the recorder was set to zero by adjusting the micrometer and then the lamp intensity was increased to normal and the deflection again reduced to zero. The instrument was allowed to come to thermal equilibrium and the flow was then started, the eluate passing through the hollow prism before being fed to a fraction collector. Any change in the refractive index in the eluate was indicated

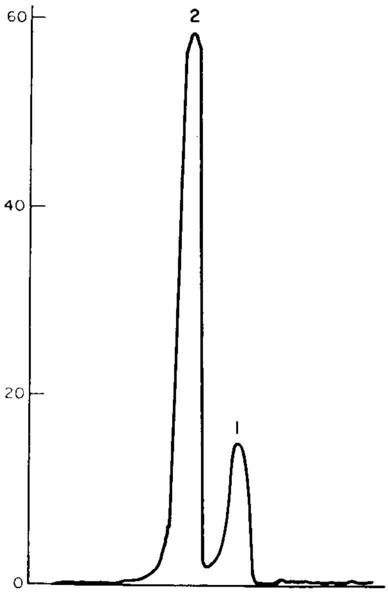

FIG. 3.—Recorder trace.
Peak 1—0·01% D-mannose solution.
Peak 2—0·05% D-mannose solution.

on the recorder and zones of eluted sample gave rise to peaks similar to those obtained with a gas chromatography apparatus (Fig. 3).

Sensitivity

The sensitivity of the instrument is determined by the brightness of the lamp and the sensitivity of the recorder. A full-scale deflection corresponding to $\Delta\mu = 10^{-4}$ was achieved with a base-line noise corresponding to $\Delta\mu = 5 \times 10^{-7}$. This means that when solutions of organic compounds in aqueous solutions are being monitored, where differences in refractive indices of 0·1 may be expected, concentrations of the order of 10 ppm may be detected.

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Summary—Light passes through a hollow prism containing the sample liquid and is then focussed on a position-sensitive photodiode. Movement of the image due to a change in the refractive index of the sample produces an electrical signal which is recorded directly on a potentiometer recorder.

Zusammenfassung—Licht durchsetzt ein Hohlprisma, das die zu untersuchende Flüssigkeit enthält, und wird dann auf eine stellungsempfindliche Photodiode fokussiert. Eine Bewegung des Bildes wegen einer Änderung des Brechungsindex der Probe erzeugt ein Signal, das direkt auf einem Potentiometerschreiber registriert wird.

Résumé—La lumière passe à travers un prisme creux contenant le liquide échantillon et est focalisée alors sur une photodiode sensible à la position. Le mouvement de l'image due à un changement dans l'indice de réfraction de l'échantillon produit un signal électrique qui est noté directement sur un potentiomètre enregistreur.

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Determination of aluminium in a "nimonic" alloy by activation with fast neutrons

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ALTHOUGH X-ray fluorescence and atomic-absorption spectroscopy are widely used for the analysis of complex matrices such as nimonic alloys, there is a continuing need for referee methods, either instrumental or classical, since interelement interference effects in X-ray fluorescence[1,2,3] and formation of non-dissociated compounds in flames[4,5,6] can give rise to difficulties.

Fast (14·7 MeV) neutron activation followed by pulse-height analysis of gamma-ray spectra offers a rapid non-destructive method for the analysis of certain elements in multi-component high temperature alloys (nimonic alloys). The composition of the alloy investigated is shown in Table I.

The nuclear properties of boron, carbon, niobium and sulphur preclude the possibilities of detection by fast neutron irradiation, and molybdenum, phosphorus, silicon, titanium and zirconium, although this method can theoretically be used (Table II),[7] cannot be detected in the quantities likely to be found in the alloy under investigation. The determination of aluminium, chromium, cobalt, iron and manganese was considered to be worthy of further study.

TABLE I.—COMPOSITION OF NIMONIC ALLOY

Element	Specification %	Chemical analysis, %	Element	Specification %	Chemical analysis, %
C	0·08–0·15	0·06	Ti	0·5–1·5	0·92
Mn	0·25 max	0·02	Al	5·5–6·5	6·34
Si	0·50 max	0·01	Fe	2·0 max	0·075
Cr	12·5–14·5	13·5	B	0·005–0·015	0·013
Ni	balance	72·5	Zr	0·05–0·15	0·10
Co	1·0 max	0·11	S	trace	0·013
Mo	3·8–5·2	4·55	P	trace	0·002
Nb + Ta	1·8–2·8	2·10			

EXPERIMENTAL

Apparatus and technique

The nimonic sample (435 mg, as turnings) in a polythene capsule 15·87 mm in diameter and 6·35 mm deep was irradiated with 14·7 MeV neutrons at a constant flux of 7 × 10^8 neutrons/sec. The capsule was pneumatically transferred to a detector consisting of a 75 × 75 mm sodium iodide crystal/photomultiplier combination. The output of the photomultiplier was fed into a 400-channel TMC analyser equipped with print-out. This analysis system has been described elsewhere.[8,9,10] The sample was irradiated for 5 min, followed by a 1-min decay period ("cooling") and a 4-min counting period.

TABLE II.—REACTIONS OF NIMONIC COMPONENTS WITH 14 MeV NEUTRONS

Element	Reaction	Isotopic abundance, %	Cross-section, *mbarn*	Product half-life	Gamma-energies, *MeV*	Interfering reactions	Cross-section *mbarn*
Aluminium	^{27}Al(n, p)^{27}Mg	100	80	9·45 min	0·83	^{30}Si(n, α)^{27}Mg	50
					1·02	^{28}Mg(n, γ)^{27}Mg	0·49
Aluminium	^{27}Al(n, p)^{24}Na	100	115	14·97 hr	1·37	^{24}Mg(n, p)^{24}Na	115
					2·75		
Cobalt	^{59}Co(n, α)^{56}Mn	100	30	2·58 hr	0·845	^{53}Mn(n, γ)^{56}Mn	0·76
					1·81	^{56}Fe(n, p)^{56}Mn	130
Chromium	^{52}Cr(n, p)^{52}V	84	80	3·76 min	1·44	^{55}Mn(n, α)^{52}V	50
	^{53}Cr(n, p)^{53}V	9·6	62	2·0 min	1·00		
Iron	^{56}Fe(n, p)^{56}Mn	92	130	2·58 hr	0·845	^{59}Co(n, α)^{56}Mn	30
					1·81	^{55}Mn(n, γ)^{56}Mn	0·76
Manganese	^{55}Mn(nα)^{52}V	100	50	3·76 min	1·44	^{52}Cr(n, p)^{52}V	80
Nickel	^{62}Ni(n, p)^{62}Co	3·66	34	13·9 min	1·17, 1·47, 1·74		
	^{58}Ni(n, p)^{58}Co	68	380	70 d	0·81		
	^{58}Ni(n, 2n)^{57}Ni	68	160	37 hr	1·37		
Silicon	^{28}Si(n, p)^{28}Al	92	250	2–3 min	1·78	^{31}P(n, α)^{28}Al	150
Molybdenum	^{97}Mo(n, p)^{97}Nb	9·45	110	72 min	0·665	^{96}Zr(n, γ)^{97}Zr	4
	^{100}Mo(n, 2n)^{99}Mo	9·62	2039	66 hr	0·74		
Phosphorus	^{31}P(n, α)^{28}Al	100	150	2·30 hr	1·78	^{28}Si(n, p)^{28}Al	250
	^{31}P(n, p)^{31}Si	100	80	2·62 hr	1·26	^{34}S(n, α)^{31}Si	130
	^{31}P(n, 2n)^{30}P	100	11	2·6 min	2·24		
Titanium	^{46}Ti(n, p)^{46}Sc	8·0	530	840 d	1·12	^{45}Sc(n, γ)^{46}Sc	
					0·89		
	^{48}Ti(n, p)^{48}Sc	74	90	44 hr	1·31	^{51}V(n, α)^{48}Sc	30
					1·04		
					0·99		
Zirconium	^{90}Zr(n, p)^{89m}Zr	51	80	4·4 min	0·59		

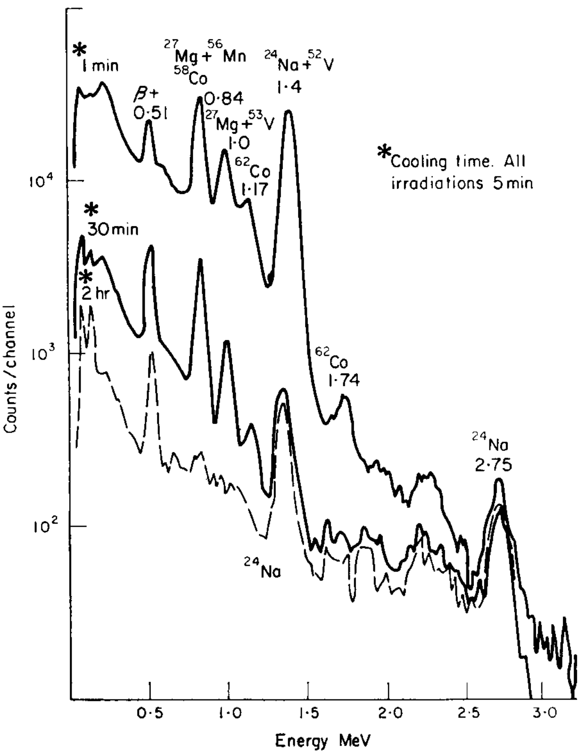

FIG. 1.—Spectra from nimonic alloy.

Typical spectra obtained by using this schedule are shown in Fig. 1.

The areas under the photopeaks were measured by the technique described by Covell.[11] The quantitative contribution of each of the elements investigated was determined by comparison of the areas under the corresponding photopeaks of specially prepared standards irradiated to the same schedule.

The standards selected were analytical grade metal salts of densities such that when the capsule was filled (by light ramming), the weight of metal corresponded as closely as possible to the weight in 435 mg of alloy. Solutions in the capsules would probably have made the best standards, but were abandoned because of difficulties in sealing the capsules.

Determination of elements

Aluminium, iron, cobalt, nickel (0·84 *MeV*). After 2 hr cooling of the irradiated sample, the area under the 0·84 MeV photopeak (Fig. 1) is small owing to decay of ^{27}Mg derived from aluminium (Table II). The residual count is due to ^{56}Mn from cobalt ($t_{1/2}$ = 2·58 hr) and ^{58}Co from nickel ($t_{1/2}$ = 70 d). Further decay leaves only the activity due to ^{58}Co, which subtracted from that after 2 hr decay gives the ^{56}Mn contribution. This, when corrected to t_0 (corresponding to the end of irradiation) and added to the ^{58}Co activity, can be subtracted from the total photopeak area to give ^{27}Mg, *i.e.*, aluminium.

The individual contributions from iron and cobalt are inseparable, since both give ^{56}Mn with fast neutrons, but an estimate of the maximum contribution from each could be made with suitable standards.

Aluminium and chromium (1·0 *MeV*). The area under this photopeak is due to ^{27}Mg from aluminium (25964 counts in Fig. 1) and ^{53}V from chromium (2967 counts, $t_{1/2}$ = 2·0 min). The great difference between the two counts and the corrections required to obtain a result make this photopeak unreliable for quantitative work.

Aluminium, chromium, manganese and nickel (1·4 *MeV*). This photopeak is due to ^{52}V ($t_{1/2}$ = 3·77 min) from chromium and manganese, ^{24}Na ($t_{1/2}$ = 14·97 hr) from aluminium, ^{62}Co ($t_{1/2}$ = 13·9 min) from nickel and ^{57}Ni ($t_{1/2}$ = 37 hr). Assuming a nickel content of 72·5%, the nickel contribution from the standard (315 mg of nickel powder) is subtracted from the remaining activity, giving the ^{24}Na contribution. This is corrected to t_0 and compared with aluminium standards (Table III) to give the aluminium content.

TABLE III.—ALUMINIUM DETERMINATION

Al in standard* *mg*	Photo-peak energy, *MeV*	Al in 435 mg of alloy, *mg*	Al in alloy, %
27·71	0·84	35·6	8·2
30	0·84	30·1	6·9
27·71	1·0	31·0	7·1
30	1·0	37·0	8·5
27·71	1·4	34·7	8·0
30	1·4	29·9	6·9

Supplier's analysis: 6·34%; 27·6 mg in 435 mg of alloy. Spec. max. 6·50% (28·28 mg).

* N.B. (1) All standards ammonium alum.

(2) An attempt to use aluminium oxide as a standard gave 19 mg of aluminium in 435 mg of alloy (0·84 MeV photo-peak).

If the specified maximum manganese content (0·25%) is assumed present, the manganese count from the standard (manganese sulphate) is only 0·44% of the total area under the photopeak. If the nickel and aluminium contributions are subtracted from the total photopeak area, the resultant count, when compared with the chromium standard (Table IV), gives a figure for chromium, the manganese contribution being ignored.

TABLE IV.—CHROMIUM DETERMINATION

Standard (Cr, 59 mg)	Photo-peak energy, *MeV*	Cr in 435 mg of alloy, *mg*	Cr in alloy, %
Chromic oxide	1·0	43·6	10·0
Chrome alum	1·0	46·2	10·6
Chromic oxide	1·4	68·7	16·0
Chrome alum	1·4	82·7	19·0

Supplier's analysis: 13·5%; 58·72 mg in 435 mg of alloy. Spec. max. 14·5% (63·08 mg).

RESULTS

Only the results for aluminium can be said to be quantitative (Table III). The specific activity (^{27}Mg) generated in chemically identical standards, shows no dependence on aluminium content, and variations are almost certainly due to differences in packing geometry. An improvement may be made by pelleting in a press before irradiation. The precision of the results (standard deviation

$\pm 2{\cdot}9$ mg, coefficient of variation $\pm 8{\cdot}7$%) compares well with an atomic-absorption study.[12] The results were all higher than the supplier's analysis (wet chemical) and the specification maximum.

The results obtained for chromium from the 1·4 MeV photopeak are shown in Table IV. There was a difference of 17% in the specific activities (^{52}V) generated in the chromic oxide and chrome alum standards, leading to a 23% difference in the results for chromium. This highlights the importance of finding suitable standards.

No separate figures could be obtained for iron and cobalt for reasons outlined above. Nickel is not of interest in the analysis of nickel-base alloys, but the ^{58}Co peak at 0·81 MeV ($t_{1/2}$ = 70 d) would enable nickel to be determined in cobalt-base alloys. The low level of the ^{52}V activity from manganese renders it valueless for quantitative work in the particular alloy under investigation.

CONCLUSIONS

It has been shown that aluminium at the 6% level in a complex matrix such as a nimonic alloy can be determined non-destructively by activation with fast neutrons with a precision comparable to that obtainable by atomic-absorption spectroscopy (5–10%). The determination of chromium at the 13–14% level shows promise, but the problem of finding suitable standards has so far resulted in relatively poor figures. Activation of manganese and nickel standards gave well defined photopeaks, and these elements, if present in sufficient amounts, could be determined in complex matrices.

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Summary—Aluminium at the 6% level was determined in a 15-component "nimonic" alloy with a coefficient of variation of $\pm 8{\cdot}7$% by using fast-neutron activation followed by pulse-height analysis of gamma-ray spectra. The possibility of determining chromium, iron, cobalt and manganese is discussed.

Zusammenfassung—Aluminium im Bereich um 6% wurde in einer "nimonic"-Legierung aus 15 Komponenten mit einem Variationskoeffizienten von ±8,7% bestimmt. Es wurde mit schnellen Neutronen aktiviert und die Gammaspektren im Impulshöhenanalysator gemessen. Die Möglichkeit, Chrom, Eisen, Kobalt und Mangan zu bestimmen, wird diskutiert.

Résumé—On a déterminé l'aluminium à la teneur de 6% dans un alliage "nimonique" à 15 constituants avec un coefficient de variation de ±8,7% en utilisant l'activation par neutrons rapides suivie d'analyse de hauteur d'impulsion des spectres de rayons gamma. On discute de la possibilité de doser le chrome, le fer, le cobalt et le manganèse.

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Photometrische Bestimmung von Gold mit Anthranilsäure

(*Eingegangen am* 24. *Mai* 1968. *Angenommen am* 19. *Juni* 1968)

Bei der Untersuchung der elektrochemischen Eigenschaften dünner Goldschichten war die Erfassung der totalen Goldmenge erforderlich, um genaue Aussagen über die Schichtdicke zu ermöglichen. Folgende Anforderungen an ein Bestimmungsverfahren wurden gestellt: Schnelle und genaue Methode; Anwendungsbereich von 50–1000 µg; Bestimmung in Gegenwart des zum Lösen der Schichten erforderlichen Königswassers. Eine diesen Forderungen entsprechende Methode wurde in der Literatur bisher nicht beschrieben.[1,2] Das eventuell in Frage kommende Reduktionsmittel Chlorpromasin[3] hat den Nachteil, psychotrope Wirkungen hervorzurufen. Weiterhin werden bei diesem Verfahren große Reagensmengen verbraucht.

Daher wurde ein neues photometrisches Verfahren zur Goldbestimmung ausgearbeitet, wobei Anthranilsäure zur Bildung eines Goldsols verwendet wird. Anthranilsäure in salzsaurer, alkoholischer Lösung wurde schon von Popa[4] zur Reduktion von Gold benutzt.

EXPERIMENTELLER TEIL

Reagenzien

Goldeichlösung: 495 µg/ml. Es wird 49,5 mg Gold (Reinheitsgrad 99,98 %) in 4 ml Königswasser gelöst und mit destilliertem Wasser auf 100 ml aufgefüllt.

Anthranilsäurelösung: 4-%ige Lösung in Äthanol (= 0,292*M*). Die Lösung wird im Dunkeln aufbewahrt.

Königswasser wird durch Mischen von 3 Volumenteilen Salzsäure (d = 1,19) und 1 Volumenteil Salpetersäure (d = 1,42) unmittelbar vor Gebrauch hergestellt, da ein hoher Chlorgehalt die Ergebnisse verfälscht.

Pufferlösung: 12,6 g Zitronensäure ($C_6H_8O_7 \cdot H_2O$) und 35,25 g Natriumcitrat ($C_6H_5O_7Na_3 \cdot 2H_2O$) werden in destilliertem Wasser zu 100 ml gelöst. Die entstehende Lösung ist 1,2*M* an Natriumcitrat und 0,6*M* an Zitronensäure. Die Konzentration des Puffers ist so gewählt, daß in der Meßlösung ein pH von 4,1 herricht.

Arbeitsanleitung

Zum Lösen einer Goldprobe gibt man aus einer Mikrobürette genau 0,600 ml frisch bereitetes Königswasser, bringt diese Lösung mit etwa 10 ml destilliertem Wasser in einen 25 ml Meßkolben, versetzt mit 10 ml Pufferlösung und gibt 2 ml 4%ige äthanolische Anthranilsäurelösung hinzu. Nach dem Umschütteln füllt man sofort mit dest. Wasser bis zur Eichmarke auf; 10–12 Min nach Zugabe der Anthranilsäure wird die Extinktion des Goldsols bei 440 nm gemessen.

Das Absorptionsspektrum des bei pH = 4,1 erzeugten Goldsols gibt Abb. 1 wieder. Die Extinktion hängt stark vom pH-Wert ab (Abb. 2). Sie erreicht nach etwa 10 Min. einen über längere Zeit konstanten Maximalwert (Abb. 3) bis das Gold nach mehreren Stunden schließlich ausflockt. Den Einfluß der Reagenzmenge auf die Absorption der Goldlösung zeigt Abb. 4.

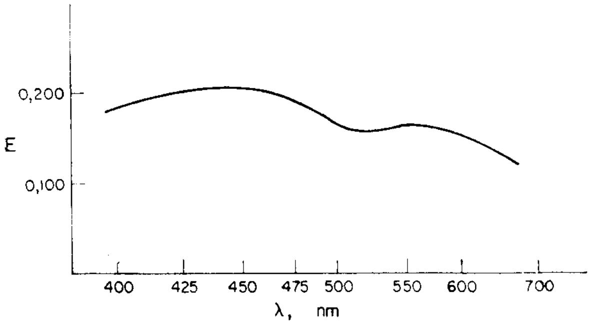

Abb. 1—Absorptionsspektrum des Goldsols. 495 μg Au, pH = 4.1.

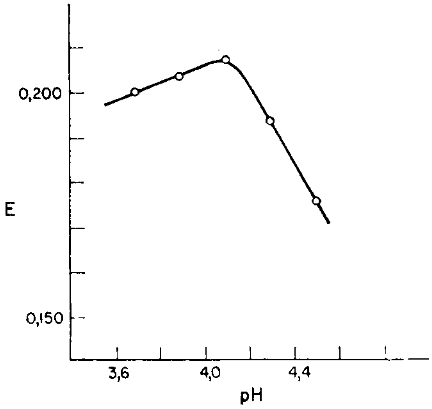

Abb. 2—Abhängigkeit der Extinktion des Goldsols vom pH. 247 μg Au, λ = 440 nm.

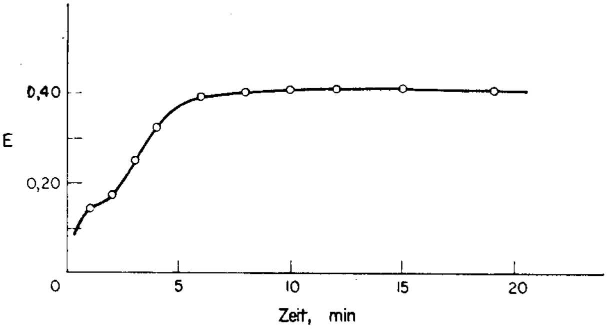

Abb. 3—Änderung der Extinktion des Goldsols mit der Zeit. 495 μg Au, λ = 440 nm, pH = 4,1.

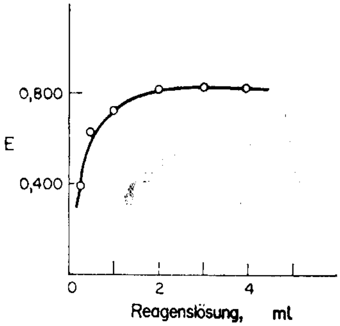

ABB. 4—Einfluß der Reagenzmenge auf die Extinktion des Goldsols.
990 μg Au, λ = 440 nm, pH = 4,1
E nach 20 Min. gemessen.

Das Lambert-Beersche Gesetz ist im Konzentrationsbereich von 2,0–50 μg/ml erfüllt. Eine vorgegebene Goldmenge von 495 μg/ml kann mit einer Genauigkeit von ±3% bestimmt werden.

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Zusammenfassung—Eine photometrische Methode zur Bestimmung von Gold als Kolloidgold wird beschrieben. Als Reduktionsmittel dient Anthranilsäure. Die Methode ist einfach, schnell und hat den Vorteil, in Gegenwart des zum Lösen des Goldes erforderlichen Königswassers anwendbar zu sein. Totalgoldmengen von 50–1000 μg können bestimmt werden.

Summary—A colorimetric method is described for the determination of gold as a colloidal solution, with anthranilic acid as reducing agent. The method is rapid and simple, and has the advantage of working in the presence of *aqua regia* used to dissolve the gold. Quantities of 50–1000 μg of gold may be determined.

Résumé—On présent une méthode colorimétrique pour le dosage de l'or en état colloïdal, utilisant comme réactif de reduction l'acide anthranilique. La méthode est simple, rapide, et présent l'avantage de pouvoir être utilisée en présence de l'eau régale employée pour la solubilisation de l'or. Quantités totales de 50–1000 μg d'or peuvent être dosée.

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Radiometric acid–base titrations

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THE radiometric titration principle invented by Langer[1] has recently acquired importance. Originally, the method could only be used for two-phase titrations, the first applications being to precipitation titrations. Later it was also used in extraction titrations, where it was especially effective since it made possible the successive titration of several ions in the same solution. Extraction titrations are usually based on complex formation, but direct radiometric complexation titrations can be performed without extraction by means of "phase-changing" indicators. These are labelled substance which begin to transfer from one phase to another at the end-point.[2]

Phase-changing indicators have recently been used in radiometric redox titrations,[3,4] and the principle can also be used in acid–base titrations, especially with dark or opaque solutions, or solutions containing fluoride ions.

If a suitable labelled metal salt is added to an acid to be titrated with base, the metal hydroxide will begin to precipitate at the end-point. The activity of the solution is constant until the end-point and linearly decreases after it. The converse holds for the reverse titration.

The choice of the metal salt is governed by the pH at the end-point. In the titration of a strong acid or base, any metal salt can be used of which the hydroxide begins to precipitate within a suitable pH range. In the titration of weak acids the hydroxide of the metal must begin to precipitate above pH 7. A smaller excess of titrant is needed to form or dissolve the hydroxide if a univalent cation is used.

Enough metal salt must be used for a sufficient number of points to be obtained after the equivalence point for the titration curve to be drawn, especially if the metal can form soluble hydroxo-complexes (e.g. Fig. 1*a*, where the activity increases after a second break-point because of formation of tetrahydroxozincate).

It is often difficult to obtain a neutral solution of an otherwise suitable metal ion. Sometimes a known amount of acid is added to the indicator solution and a correction applied. We have found it more expedient to add the inactive metal salt in solid form, and its radioisotope in solution; the acidity of the latter is then negligible.

Another type of phase-changing redox indicator gives precipitation of the elementary metal at the end-point, *e.g.*, ^{110}Ag or ^{203}Hg labelled salts in ascorbic acid reductions.

EXPERIMENTAL

Titrations were carried out by two methods, without special apparatus.

Batch method

Equal volumes of the acid solution were placed in separate volumetric flasks, equal amounts of the indicator and increasing amounts of standard base solution were added, and the solutions were diluted to volume with water, mixed and centrifuged. The activities of equal volumes of the solutions were measured in a test-tube placed in an NaI(Tl) well-crystal. The activities were plotted against the volume of standard solution added. A typical curve is shown in Fig. 1*a*.

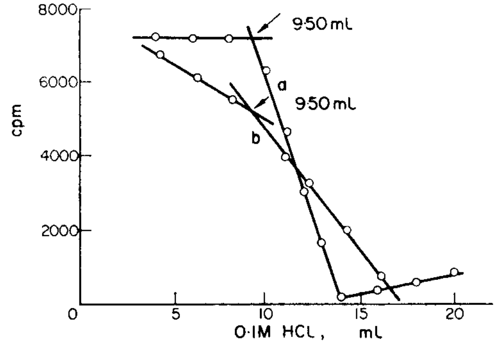

FIG. 1—*a*—Batch titration of 0·1*M* HCl, with 2 ml of 0·1*M* ^{65}Zn-labelled ZnCl$_2$ (previously neutralized to visual end-point) as indicator; phenolphthalein end-point at 9·52 ml. *b*—Continuous titration of 0·1*M* HCl (9·52 ml), with 40 mg of ZnCl$_2$ and and tracer amount of ^{65}ZnCl$_2$ solution as indicator.

Continuous titration

The activity of the solution was determined after each addition of standard solution. When the precipitation had started, the solution was centrifuged, the activity measured, and the solution returned to the titration flask for further titration. The higher the specific activity of the metal salt used, the steeper the curve after the equivalence point, and the sharper the break-point.

A typical curve is shown in Fig. 1*b*. The results of 6 replicate titrations were: 9·60, 9·50, 9·45, 9·58, 9·65, 9·50 ml: mean 9·55 ml.

Figure 2 shows the continuous titration of base with acid.

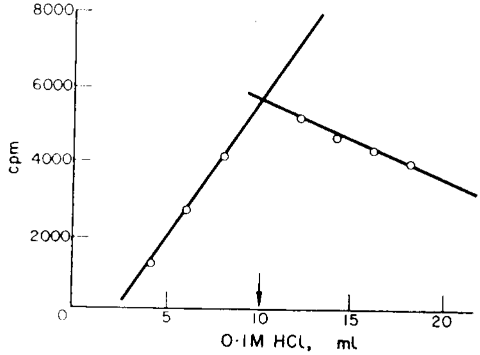

FIG. 2—Titration of 0·1*M* NaOH, with 2 ml of 0·05*M* neutralized labelled $ZnCl_2$ indicator; phenolphthalein end-point at 10·20 ml.

Mercury(II) and iron(III) salts labelled with ^{203}Hg and ^{59}Fe respectively, were also tried as indicators, as 0·05*M* solutions, iron(III) chloride gave less accurate results because it could not be neutralized and its acidity could not be determined accurately enough.

Neither indicator was satisfactory in 0·01*M* concentration.

Acknowledgement—We express our thanks to Miss K. Éber and Mrs. G. Kasszán for their help with the experimental work.

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Summary—Acid-base titrations can be performed with radiometric end-point detection by use of labelled metal salts (*e.g.*, $ZnCl_2$, $HgCl_2$). Owing to the formation or dissolution of the corresponding hydroxide after the equivalence point, the activity of the titrated solution linearly increases or decreases as excess of standard solution is added. The end-point of the titration is determined graphically.

Zusammenfassung—Säure-Basen-Titrationen mit radiometrischer Endpunktsanzeige können mit Hilfe markierter Metallsalze (z.B. $ZnCl_2$, $HgCl_2$) ausgeführt werden. Wegen der Bildung oder Auflösung des betreffenden Hydroxids nach dem Äquivalenzpunkt steigt oder fällt die Aktivität der titrierten Lösung beim Zusak von überschüssiger Messlösung Der Endpunkt der Titration wird graphisch bestimmt.

Résumé—On peut réaliser les titrages acide-base avec détection radiométrique du point d'equivalence utilisant des sels de métaux marqués (par ex., $ZnCl_2$, $HgCl_2$). A cause de la formation ou de la dissolution de l'hydroxyde correspondant après le point d'équivalence, l'activité de la solution titrée croît ou décroît linéairement par addition d'excès de solution étalon. On détermine graphiquement le point d'equivalence.

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New chromogens of the ferroin-type—IV
Oximes of substituted methyl and phenyl 2-pyridyl ketones

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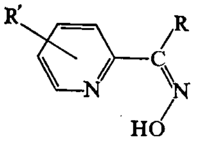
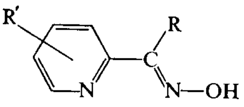
RELATIVELY few compounds in which an oxime group is incorporated as part of the ferroin group —N=C—C=N— have been investigated as chromogenic reagents. The oximes of phenyl 2-pyridyl ketone[1–5], methyl 2-pyridyl ketone[6], pyridine-2-aldehyde[7,8] and 6-methylpyridine-2-aldehyde[9] have been studied most extensively. The first three compounds are noteworthy for their ability to form extractable iron(II) chelates in strongly alkaline solution. The fourth compound forms an extractable copper(I) complex in strongly alkaline solution. The favourable alkaline stability of the complexes is probably associated with the negative charge on the ligands which results on ionization of the oxime hydrogen atom[8]. Another interesting aspect is the possible existence of *syn*- and *anti*-stereoisomers, depicted as follows:



anti-isomer
(*anti*-configuration of R and OH)



syn-isomer
(*syn*-configuration of R and OH)

Limited evidence to date suggests that only the *syn*-isomer of ferroin-type oximes may be capable of metal ion chelation. Tschugaeff[10] found that only the lower melting isomer of phenyl 2-pyridyl ketone oxime gave coloured metal complexes. Huntress and Walter[11] later demonstrated that this isomer was in fact the *syn*- rather than the *anti*-isomer originally postulated by Tschugaeff. Recently Case and McMenamin[12] found that only the *syn*-isomers of certain 2-pyridyl ketone oximes would form coloured chelates with iron(II).

In this investigation some newly synthesized oximes of substituted methyl and phenyl 2-pyridyl ketones, provided by Professor F. H. Case of Temple University, were examined with regard to their chelation tendencies toward iron(II), copper(I), and other first-row transition metal ions. Objectives were to discover any differences in chelation tendencies between the *syn*- and *anti*-isomers, to evaluate the effects of various substituents on chromogenic properties, and to examine the influence of oxime deprotonation (ligand ionization) on spectral properties of the chelates in the hope, as in previous studies in this series,[13] of finding superior chromogenic reagents.

EXPERIMENTAL

Samples of the oximes, for which preparative and analytical details have been recently published[12], were kindly provided by F. H. Case. The compounds, identified by Roman numerals, and their configurations are given in Table I.

Descriptions of the various standard solutions, pH buffers, reagents, and procedures appear in an earlier paper of this series.[13] Solutions prepared for recording the NMR spectra (using a Varian A-60 instrument) contained 1–2 mole% of the oxime in dimethylsulphoxide. Ethanol was used as the solvent to prepare 0.01*M* solutions of the oximes for colour tests and spectrophotometric studies. Solutions of the transition metal ions for colour reaction tests were 0.01*M*. Freshly prepared 10% solutions of sodium dithionite were used instead of hydroxylamine hydrochloride for preparing strongly alkaline solutions ($\text{pH} > 11$) of the iron(II) chelates.

Absorption characteristics of the iron(II) chelates, extracted from 4*M* sodium hydroxide into isoamyl alcohol, were determined by the following procedure. Weighed amounts of standard iron solution were delivered into small beakers from a weight-burette. To each were added 5 ml of 5*M* sodium hydroxide, 1 ml of sodium dithionite solution, and 1 ml of 0.01*M* oxime solution. The solutions were heated for 5 min at 90–100°, cooled and extracted with a 6-ml portion of isoamyl alcohol and again with a 2-ml portion. The combined extract was diluted to volume with ethanol

TABLE 1.—COMPOUNDS STUDIES, AND CHEMICAL SHIFTS OF THE OH PROTON*

Number	Oxime of	Isomer	δ, *cps*
I	2-Acetyl-4-methyl-pyridine	*syn*-methyl	682
II	2-Acetyl-4-ethyl-pyridine	*syn*-methyl	681
III	2-Acetyl-4-phenyl-pyridine	*syn*-methyl	689
IV	2-Acetyl-4-methoxy-pridine	*syn*-methyl	685
V	2-Acetyl-6-methyl-pyridine	*syn*-methyl	680
VI	2-Acetyl-6-phenyl-pyridine	*syn*-methyl	689
VII	2-Benzoyl-4-methyl-pyridine	*syn*-phenyl	689
VII-a	2-Benzoyl-4-methyl-pyridine	*anti*-phenyl	685
VIII	2-Benzoyl-4-ethyl-pyridine	*syn*-phenyl	688
VIII-a	2-Benzoyl-4-ethyl-pyridine	*anti*-phenyl	684
IX	2-Benzoyl-4-phenyl-pyridine	*syn*-phenyl	697
IX-a	2-Benzoyl-4-phenyl-pyridine	*anti*-phenyl	689
X	2-Benzoyl-6-methyl-pyridine	*syn*-phenyl	—
X-a	2-Benzoyl-6-methyl-pyridine	*anti*-phenyl	—
XI	2-Benzoyl-6-phenyl-pyridine	*syn*-phenyl	698

* Shifts measured relative to the ^{13}CH satellite of dimethylsulphoxide at 221 cps but reported relative to tetramethylsilane. All measurements made at 40°C, the ambient temperature.

in a 10-ml volumetric flask. Spectra were recorded with a Cary Model 14 spectrophotometer and corrected for absorbance due to reagent blanks. Replicate determinations demonstrated conformance to Beer's law by each iron(II) chelate over at least a 10-fold concentration range.

Absorption characteristics of the metal chelates in aqueous ethanol solutions were determined as described in an earlier paper.[13]

RESULTS AND DISCUSSION

The NMR spectra of the oximes were examined to gain additional evidence concerning their structures. Studies by Kleinspehn, Jung and Studniarz[14] indicate that the OH proton chemical shifts for *syn*- and *anti*-isomers of oximes are slightly different, the *syn*-isomer consistently giving the greater shift. The results in Table I are thus meaningful in two respects. First, since only one OH proton signal was observed for each oxime sample, no sample contained both isomers. Second, the greater proton shift for **VII**, **VIII**, or **IX** compared with that for the respective isomers **VII-a**, **VIII-a**, or **IX-a** indicate that the former are the *syn*- and the latter are the *anti*-isomers. Hence, the NMR data corroborate the structural assignments deduced by Case and McMenamin.[12]

None of the *anti*-isomers gave coloured products at any pH with iron(II), cobalt(II) or copper(I). All of the *syn*-isomers gave colours with copper(I). Coloured products with iron(II) and with cobalt(II) were given by all of the *syn*-isomers except **V**, **VI**, **X**, and **XI**. None of the oximes formed colours with Ti(II), Ti(III), V(V), V(IV), Cr(III), Cr(IV), Mn(II), or Ni(II). It is concluded that the structure of the *anti*-isomers is not suitable for metal ion chelation. A simple test to distinguish between *syn*- and *anti*-isomers is thus indicated: the former yields a coloured copper(I) complex, but the latter does not. The failure of the *syn*-isomers **V**, **VI**, **X**, and **XI**, to form highly coloured iron(II) or cobalt(II) complexes is probably a consequence of the bulky methyl or phenyl substituents in position-6 of the pyridyl ring in these compounds. Such groups severely discourage full co-ordination of three ferroin-type ligands in an octahedral configuration about iron(II) or cobalt(II). Similar steric hindrance does not arise in the chelation of copper(I) because only two ligands are required, and their tetrahedral arrangement about copper(I) does not give rise to mutual crowding or strain.

Some properties of the iron(II) chelates are presented in Table II. All are stable in strongly alkaline medium and extractable into isoamyl alcohol. Spectral characteristics vary considerably with pH and solvent. Molar absorptivities are greatest when the chelates are extracted into isoamyl alcohol from sodium hydroxide solutions. The pronounced enchancement in the absorptivities on

TABLE II.—PROPERTIES OF THE IRON(II) CHELATES

Oxime	Chelate colour	pH Range of colour formation	Spectral characteristics In EtOH–H_2O λ, *nm*	ε	pH	In isoamyl alcohol (NaOH)* λ, *nm*	ε
I	Orange-red	4–15	529	8100	7	541	14000
			540	9200	13		
II	Orange-red	4–15	531	8300	7	543	15100
			543	10400	13		
III	Purple	3–15	548	12300	7	568	23400
			566	13300	13		
IV	Orange-red	4–15	531	7300	7	543	11900
			541	8500	13		
VII	Red	4–15	534	8200	7	546	15900
			546	10100	13		
VIII	Red	4–15	535	9200	5	548	16500
			546	11300	13		
IX	Purple	4–15	551	13100	5	566	25700
			566	14900	13		

* Chelates extracted from 4*M* NaOH.

going from aqueous to isoamyl alcohol solution is indeed remarkable and worthy of further study Deprotonation of the oxime ligands with increasing pH is accompanied by bathochromic shifts and hyperchromaticity. The most effective substituent for promoting chromogenic sensitivity is the phenyl group, at either the oxime carbon atom or at the 4-position in the pyridyl moiety. Compounds **III** and **IX**, although expensive and difficult to synthesize, are highly recommended as chromogenic reagents for determining iron in strongly alkaline materials. Either compound is superior in sensitivity to *syn* phenyl 2-pyridyl ketone oxime[4] or 4,7-dithydroxy-1,10-phenanthroline,[15] both of which have been recommended for use in strong base.

TABLE III.—PROPERTIES OF THE COPPER(I) CHELATES

Oxime	Chelate colour	pH Range for max. colour	Spectral characteristics in EtOH-H_2O λ, *nm*	ε	pH
I	Yellow	4–7	409	5300	5·2
II	Yellow	4–7	410	5800	5·2
III	Orange	4–5	430	9700	4·5
IV	Orange	4–7	400	4000	5·2
V	Yellow	4–11	422	8400	7·0
VI	Orange	3–11	422	3500	7·0
VII	Orange	4–7	422	8400	4·5
VIII	Orange	4–7	425	10000	4·5
IX	Orange	3–7	441	13800	4·5
X	Yellow	4–11	432	9100	5·2
XI	Orange	2–11	429	4900	5·2

Results for the copper(I) chelates are listed in Table III. The molar absorptivities of the copper chelates do not exhibit the marked dependence on pH or solvent that the iron(II) chelates do. The yellow copper chelates form in strongly alkaline solution but fade on standing, due to air oxidation. Ascorbic acid is somewhat more effective as a reductant than hydroxylamine in strong base, but it is not entirely adequate as protection against atmospheric oxidation on prolonged exposure. All of the copper chelates are extractable into isoamyl alcohol. The most sensitive copper chromogen is compound IX. Again it is found that phenyl substituents are the most effective for enhancing molar absorptivities. None of the chromogens, however, is superior to bathocuproine, which is widely used for the determination of microamounts of copper.[18]

TABLE IV.—PROPERTIES OF THE COBALT(II) CHELATES

Oxime	Chelate colour	pH Range for max. colour	Spectral characteristics in EtOH-H_2O		
			*λ, nm**	ε*	pH
I	Yellow	4–11	325	11800	7·0
II	Yellow	4–11	325	11900	7·0
III	Yellow	4–11	338	16500	7·0
IV	Yellow	4–11	319	13500	7·0
VII	Yellow	4–11	334	12100	5·2
VIII	Yellow	4–11	341	12400	4·5
IX	Yellow	3–11	350	15600	5·2

* Shoulder on side of absorption band of the free ligand, before reagent blank absorbance becomes significant.

The cobalt(II) chelates absorb strongly in the near ultraviolet; however, their absorption bands lie close to those of the free ligands, which are even more intense. If the solutions are made strongly alkaline, the free ligand bands and the chelate bands move closer together. The former undergo the greater bathochromic shift. Although their molar absorptivities are high (see Table IV), the cobalt(II) chelates are not particularly promising for the spectrophotometric determination of cobalt, because the corresponding copper and iron chelates absorb very strongly in the same ultraviolet region.

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Summary—The spectral characteristics, and solution conditions requisite for formation, of the iron(II), cobalt(II), and copper(I) chelates of some newly synthesized oximes containing the ferroin functional grouping have been determined. For some of the oximes, both *syn*- and *anti*-isomers were available for study. NMR spectra of the isomers differed, enabling structural distinctions to be made. None of the *anti*-isomers formed coloured metal chelates. A practical method for distinguishing between the isomers can be based on these findings. Two of the compounds proved very promising as highly sensitive chromogens for determining iron in strongly alkaline materials.

Zusammenfassung—Die spektralen Eigenschaften der Chelate von Eisen(II), Kobalt(II) und Kupfer(I) mit einigen neu synthetisierten Oximen, die die funktionelle Gruppierung des Ferroins enthalten, wurden ermittelt, sowie die Lösungsbedingungen, die zu ihrer Bildung notwendig sind. Für einige der Oxime waren zu der Untersuchung sowohl die *syn*- als auch die *anti*-Isomeren verfügbar. Die NMR-Spektren der Isomeren waren verschieden, sodaß die Strukturunterscheidung möglich war. Kein *anti*-Isomeres bildete farbige Metall-Chelate. Eine praktische Methode zur Unterscheidung der Isomeren kann darauf gegründet werden. Zwei der Verbindungen zeigten sich sehr vielversprechend als hochempfindliche Farbreagentien zur Bestimmung von Eisen in stark alkalischem Material.

Résumé—On a déterminé les caractéristiques spectrales et les conditions de solution nécessaires à la formation des chélates de quelques oximes nouvellement synthétisées contenant le groupement fonctionnel ferroïne avec les fer(III), cobalt(II) et cuivre(I). Pour quelques-unes des oximes, les deux isomères *syn* et *anti* étaient disponibles pour l'étude. Les spectres RMN des isomères diffèrent, permettant de faire des distinctions structurales. Aucun des isomères *anti* ne forme de chélates métalliques colorés. On peut baser une méthode pratique de distinction des isomères sur ces découvertes. Deux des composés se sont révélés très prometteurs comme chromogènes hautement sensibles pour la détermination du fer dans les produits fortement alcalins.

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EDTA titration of tellurium, based on the formation of copper(I) telluride

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THE increasing development and use of thermoelectric devices have focused attention on the determination of tellurium. Unfortunately, there are few analytical methods reported in the literature from which to choose. Kodama[1] gives a summary of the important chemical methods used to determine the element, including the use of organic precipitants and colorimetric methods.

The determination of tellurium by reduction to the element with sulphur dioxide and hydrazine is perhaps the most commonly used method, but the complete recovery of colloidal particles of tellurium can be difficult. The elements that are easily reduced to the elemental state are often found coprecipitated with tellurium. Cheng[2,3] found that some of these difficulties are avoided by precipitating tellurium as tellurous acid in the presence of EDTA. Nonova and Tuzsuzova[4] have developed an indirect EDTA titrimetric method to determine 50–350 μg of tellurium. The method is based on the initial reaction between tellurium(IV) and diethyldithiocarbamic acid in a liquid-liquid extraction system. The method involves many manipulations and would not be suitable for the determination of tellurium in thermoelectric materials.

The determination of tellurium described in this paper is based on the quantitative and stoichiometric precipitation of copper(I) telluride. The compound is filtered off and dissolved, and the copper titrated with EDTA, Murexide being used as visual indicator. The method should have wide application due to its simplicity and selectivity. Although discovered independently, the method is similar to that of Nonova[5] for selenium.

EXPERIMENTAL

Reagents

Copper(II) chloride solution. Prepared by adding 13 g of the dihydrate to 100 ml of concentrated hydrochloric acid and diluting to 1 l. with water.

Tellurium powder. Electronic grade.

Sodium hypophosphite. Reagent grade monohydrate.

EDTA solution, 0·0500M. Prepared from reagent grade disodium ethylenediaminetetra-acetate dihydrate and standardized against pure copper.

Murexide powder.

General procedure

Transfer the weighed tellurium alloy to a 250-ml beaker. Add 5 ml of *aqua regia* and warm on the hot-plate to dissolve the sample. Cool and add 5 ml of sulphuric acid. Evaporate carefully till sulphur trioxide fumes appear. Cool, and wash the sides of the beaker sparingly with water. Evaporate the sample again until copious sulphur trioxide fumes are formed. Cool and add 110 ml of the copper(II) chloride solution. Warm if necessary to dissolve the salts. Cool the solution to room temperature and add 5 g of sodium hypophosphite monohydrate. With occasional stirring, bring the suspension to the boil. Filter immediately through medium porosity 9-cm diameter filter paper. The use of filter pulp is desirable. Wash thoroughly with boiling water; it is important to wash the mother liquor from the precipitate as quickly as possible to prevent decomposition of the precipitate. Transfer the black precipitate and filter paper back to the original beaker. Add 15 ml of 15% nitric acid. Break up the filter paper with a stirring rod to aid in the decomposition of the precipitate. Warm gently until no black particles are detected. Add 50 ml of water and filter through 11-cm filter paper. Collect the filtrate in a 500-ml Erlenmeyer flask and wash thoroughly with water. Add water to bring the volume of the filtrate to 300 ml. Add concentrated ammonia solution dropwise until all the tellurous acid is dissolved. The solution should be slightly basic and have a blue colour. Avoid a large excess of ammonia. Add approximately 7 mg of Murexide and titrate with 0·0500*M* EDTA. The end-point is reached when 1 extra drop of titrant produces no visible colour change. 1 ml of 0.0500*M* EDTA is equivalent to 3·190 mg of tellurium.

Procedure if As, Hg, Sb, *and* Se *are present*

Follow the general procedure through the first sulphuric acid fuming. Then cool the sample and add 15 ml of hydrobromic acid. Carefully evaporate until dense sulphur trioxide fumes appear. Cool the sample and add 3 ml of nitric acid. Evaporate the sample to sulphur trioxide fumes. Cool, wash down the sides of the beaker with water, and again evaporate the sample to sulphur trioxide fumes. Resume the general procedure with the cooling and adding of 110 ml of the copper(II) chloride solution.

RESULTS AND DISCUSSION

Table I shows the results obtained with synthetic samples containing 50 mg of tellurium together with diverse elements in order to detect possible interferences. Results showed a standard deviation of 0·3 mg.

Table II represents the results of assays of various thermoelectric materials by three analysts. Results are in good agreement.

Choice of reducing agent

Hydrazine hydrochloride, sodium dithionite, sodium hypophosphite, and tin(II) chloride were tried as possible reductants in the precipitation of copper(I) telluride, Cu_2Te. Only sodium hypophosphite yielded quantitative results. Tin(II) chloride was second best, with a 90% recovery of tellurium. The precipitating conditions were identical to those in the general procedure. Chemical analyses of the Cu_2Te precipitates confirm the stoichiometry.

It was found that on addition of sodium hypophosphite to a hot acidified solution of Cu(II) and Te(IV) some tellurium was lost as hydrogen telluride, causing low results. The speed of this reaction

TABLE I.—RECOVERY OF TELLURIUM FROM SYNTHETIC MIXTURES

100 mg of each element* added to 50·0 mg of Te	Te found, *mg*	Relative error, %
Ag†	49·4	1·2
Al	50·0	0·0
As†	49·5	1·0
Au	49·6	0·8
Be	49·9	0·2
Bi	50·2	0·4
Ca	50·0	0·0
Cd	49·5	1·0
Co	49·5	1·0
Cr	50·0	0·0
Fe	50·2	0·4
Ga	50·2	0·4
Hg†	49·6	0·8
In	50·0	0·0
Mg	50·4	0·8
Mn	49·7	0·6
Mo	49·5	1·0
Ni	49·8	0·4
Pb	50·2	0·4
Re	50·0	0·0
Sb†	49·6	0·8
Se†	49·5	1·0
Sn	50·0	0·0
Tl	50·1	0·2
V	50·0	0·0
Zn	50·5	1·0
	Mean relative error	0·5 %
	Range	1·1 mg
	Standard deviation	0·3 mg

* All elements were added as elements except calcium and chromium, which were added as nitrates.

† Elements that were separated before the addition of sodium hypophosphite.

TABLE II.—RESULTS OF ASSAYS BY THREE ANALYSTS

Alloy	Analyst	%Te found*
ZnTe	A	66·52
	B	66·47
	C	66·63
PbTe	A	45·02
	B	45·07
	C	44·76
SnPbTe	A	44·54
	B	44·75
	C	44·49

* Each result is an average of three determinations.

is too fast if the initial temperature is too high. Tellurium was also lost when there was no excess of copper ions. These sources of error were eliminated by adding the reductant to the solution at or below room temperature and ensuring that an excess of copper was present.

Some decomposition of the Cu_2Te was noted when mother liquor was allowed to remain in an unwashed precipitate. It is believed that fine particles of the precipitate are dissolved by the residual hydrochloric acid. This can occur as the sodium hypophosphite becomes less effective in preventing oxidation when the mother liquor cools.

Interferences

Tellurous acid interfered with the copper determinations when EDTA titrations were conducted in an acidic medium. The addition of ammonia and titration at pH >7 eliminated the problem. If not separated, palladium, platinum and silver will cause low results. Silver can be separated as the chloride before the addition of sodium hypophosphite. The precipitate is washed with the copper(II) chloride solution. Gold is partially reduced to the metal by the fuming with sulphuric acid. The addition of sodium hypophosphite completes the reduction without interference in the tellurium determination. If present, thallium(I) chloride precipitates when the reducing agent is added but dissolves on heating, and therefore does not interfere.

Interference from arsenic, mercury, antimony and selenium is avoided by fuming with hydrobromic acid. No appreciable quantities of tellurium are lost if careful evaporations are carried out.

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Summary—An indirect EDTA titrimetric method is described for the determination of tellurium in thermoelectric materials and synthetic mixtures. Stoichiometric copper(I) telluride is precipitated from a hot acidic solution in the presence of excess of copper(II) chloride and sodium hypophosphite. The method is accurate (mean relative error 0.5%) and selective.

Zusammenfassung—Zur Bestimmung von Tellur in thermoelektrischem Material und in synthetischen Gemischen wird eine indirekte titrimetrische Arbeitsvorschrift angegeben. Aus einer heißen sauren Lösung wird in Gegenwart von überschüssigem Kupfer(II)-chlorid und Natriumhypophosphit stöchiometrisches Kupfer(I)-tellurid ausgefällt Die Methode ist genau (mittlerer relativer Fehler 0,5%) und selektiv.

Résumé—On décrit une méthode titrimétrique indirecte par l'EDTA pour le dosage du tellurium dans des matériaux thermoélectriques et des mélanges synthétiques. Le tellurure de cuivre(I) stoechiométrique est précipité à partir d'une solution acide chaude en la présence d'un excès de chlorure de cuivre(II) et d'hypophosphite de sodium. La méthode est précise (erreur relative moyenne 0,5%) et sélective.

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Extractive photometric determination of vanadium with catechol and a tertiary amine

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THE separation and determination of microgram amounts of vanadium is very difficult because of its variability of oxidation state. Most of the reagents react only with vanadium(V), *e.g.*, 8-hydroxyquinoline, cupferron, dithiocarbamate, but simultaneously a small amount of vanadium is reduced to the quadrivalent state.[1] The same is valid for ion-exchangers. The reactions of vanadium(IV) are usually poor, especially for separations. Extraction of vanadium–catechol complexes in the presence of tetraphenylarsonium chloride has been described[2] and for photometric determination the reactions with catechol,[3–5] dinitrocatechol,[6] arsenazo I[7] or Methylthymol Blue[8] are recommended.

In some samples that may be met in analysis, traces of vanadium are present in large excesses of aluminium, titanium, iron and alkali metal salts, and correct determination is impossible. The separation of vanadium from iron, titanium and zirconium requires an alkaline fusion, leading to a similar situation. By the addition of a suitable tertiary amine to the aqueous solution of the blue catechol complex of vanadium(IV), co-ordinately bound water is replaced by the amine and the new complex becomes extractable into chloroform. The procedure using tributylamine and collidine, and the separation of traces of vanadium from excess of aluminium and alkali metal salts are described.

EXPERIMENTAL

Reagents

All chemicals were analytical grade.

Collidine, 5% v/v solution in chloroform.

Tributylamine, 1% v/v solution in chloroform.

Catechol, 20% w/v solution in water.

Vanadium solution, 0·5 *mg/ml*. Dissolve 1·15 g of ammonium metavanadate in hot water, cool and dilute to 1 litre. Dilute 10-fold (to 0·05 mg/ml) for use.

Extraction conditions

Diphenylguanidine, quinoline, cinchonine, pyridine and its methyl derivatives were qualitatively tested as extractants and tributylamine and collidine quantitatively. The effect of the pH of the original solution, and the optimal concentrations of catechol and of the amine in chloroform were examined. From Fig. 1 it is evident that the optimal pH of the solution before extraction lies within

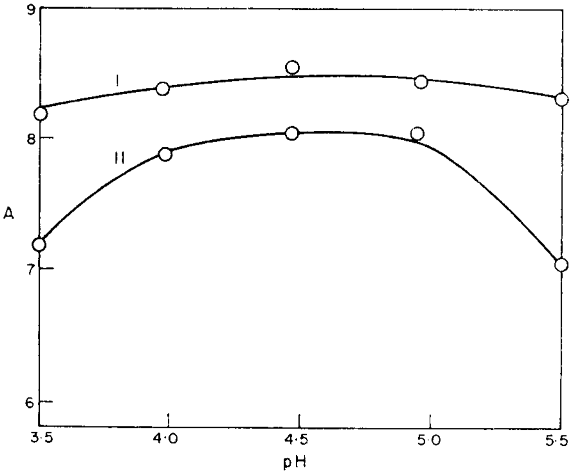

FIG. 1.—Influence of pH.
I—Tributylamine; II—Collidine

the range pH 4·2–4·8 for collidine and 3·5–5·5 for tributylamine. Tributylamine is also a better extractant than the collidine, because it gives more complete extraction of vanadium over a wide range of catechol and reagent concentrations. For complete extraction with collidine at least 1·5 g of catechol and 10 ml of 5% collidine solution in chloroform are needed for 100 ml of aqueous phase (Fig. 2) but collidine is less sensitive for extraction of traces of iron, titanium and molybdenum.

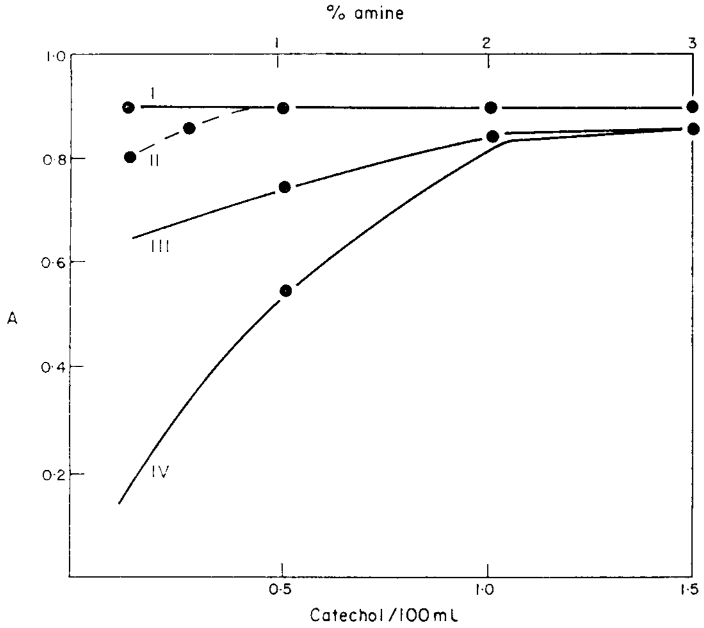

FIG. 2.—Influence of catechol and amine concentration.
I—variable tributylamine; 1·5 g of catechol
II—variable catechol; 10 ml of 2% tributylamine solution
III—variable catechol; 10 ml of 2% collidine solution
IV—variable collidine; 1·5 g of catechol

The absorption maximum of the extracted complex corresponds approximately to the maximal absorption in aqueous medium. The broad maximum lies at 590 nm for tributylamine and at 600 nm for collidine. The absorbance is constant for at least 60 min.

The influence of some foreign ions is indicated in Table I. Large excess of aluminium and traces of iron are masked by tartrate, and titanium partially by fluoride. Other ions are unreactive, or feebly extracted under the prescribed conditions, or are yellow (Ti, Mo) and so do not influence the absorbance measurement of the blue vanadium complex at 590–600 nm.

The calibration curve at 595 nm is linear for 5–80 μg of vanadium in 10 ml of chloroform (10-mm cell). The molar absorptivity is 8800 for tributylamine and 8500 for collidine; in aqueous medium it is 6800. A second extraction indicated that more than 95% of the vanadium is removed by the first extraction.

Recommended method

Evaporate to dryness 0·2–2 g of finely powdered sample mixed with 2–7 ml of hydrofluoric and 0·5–1 ml of sulphuric acid (1 + 1) in a platinum crucible and then ignite it gently. Crush the residue and fuse it with 1–5 g of sodium carbonate. Leach the melt with hot water and filter the solution after complete disintegration of the solid. Wash the residue with hot water, acidify the solution with dilute hydrochloric acid (Methyl Orange). Destroy the indicator with a few drops of bromine water. Then add ~0·1 g of sodium sulphite to reduce vanadium and evaporate the solution to 60–100 ml. Take an aliquot containing not more than 80 μg of vanadium, add 0·5 g of tartaric acid for every

TABLE I.—DETERMINATION OF 50 µg OF VANADIUM IN THE PRESENCE OF FOREIGN IONS

Vanadium found, µg	Difference, %	Ions added, *mg*	Masking agent	Extractant*
51	+2	300 Al	tartrate	T
53	+6	600 Al	tartrate	T
50	0	300 Al	tartrate	C
51	+2	0·25 Ti	fluoride	T, C
51	+2	0·5 Mo	tartrate	T
49	−2	1·5 Mo	tartrate	C
55	+10	1·6 U	tartrate	T
52	+4	0·4 U	tartrate	T
51	+2	1·6 U	tartrate	C
49	−2	2·0 W	tartrate	T
50	0	5·0 Cu	—	T
50	0	3·0 Cr	tartrate	T
49	−2	100 P_2O_5	—	T
58	+16	1·0 Fe	tartrate	T
51	+2	1·0 Fe	tartrate	C
52	+4	5·0 Fe	tartrate	C

* T = tributylamine; C = collidine.

0·1 g of aluminium and adjust to pH 4·2–4·8 with sodium acetate eventually a few drops of ammonia. Add 5 ml of 20% catechol solution (or 1 g of solid) and extract with 10 ml of 1% tributylamine or 5% collidine in chloroform. Filter the extract through a small paper filter and measure the absorbance in 10-mm cells against an extractant blank at 590–600 nm (or use an orange filter). In Table II some results of the analysis of natural samples are given.

TABLE II.—DETERMINATION OF VANADIUM IN ROCKS AND CLAYS

	Vanadium found, %			
Sample	*N*-benzoyl phenylhydroxylamine method[9,10]	Catechol methods		
		in water[3–5]	TBA	Coll
Slate	0·18	0·14	0·17	0·16
Bauxite	0·048	0·048	0·052	0·053
Clay I	0·028	0·026	0·027	0·026
Clay II	0·015	0·014	0·014	0·015
Clay III	0·0055	0·006	0·006	0·006

TBA = tributylamine; Coll = collidine method.

The method is also suitable for determination of molybdenum, uranium, titanium, niobium and tantalum. In this case EDTA can be used as a masking agent for iron.

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Summary—Metal catechol complexes can be extracted from aqueous solution with chloroform in the presence of tertiary amines, for example diphenylguanidine, tributylamine or collidine. Collidine can also be used for the determination of vanadium, titanium, molybdenum and niobium in the presence of a small amount of iron or tantalum. The method for determination of microgram amounts of vanadium is described.

Zusammenfassung—Metall-Catechin-Komplexe können aus wäßriger Lösung mit Chloroform in Gegenwart tertiärer Amine, wie z. B. Diphenylguanidin, Tributylamin oder Kollidin, extrahiert werden. Kollidin kann auch zur Bestimmung von Vanadium, Titan, Molybdän und Niob in Gegenwart kleiner Mengen Eisen oder Tantal verwendet werden. Das Verfahren zur Bestimmung von Mikrogrammengen Vanadium wird beschrieben.

Résumé—On peut extraire les complexes métalliques du catéchàl à partir d'une solution aqueuse au moyen de chloroforme en la présence d'amines tertiaires, par exemple diphénylguanidine, tributylamine ou collidine. On peut aussi utiliser la collidine pour le dosage des vanadium, titane, molybdène et niobium en la présence d'une petite quantité de fer ou de tantale. On décrit la méthode pour le dosage de quantités de vanadium de l'ordre du microgramme.

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Determination of tungsten by acidimetric titration

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THE only acid-base titrations which have been described for the determination of tungsten depend on precipitation of tungstic acid or the tungstic acid–benzidine complex, followed by dissolution of the precipitate in excess of standard alkali and back-titration of the excess.[1,2] These methods give variable results, presumably because of variation in the composition of the precipitate. Chalmers and Sinclair[3] observed that when sodium molybdate was titrated with acid in the presence of mannitol an inflection occurred in the pH titration curve at a point corresponding to the addition of one hydrogen ion per molybdate ion present. In the work described here it was found that similar behaviour occurs with the tungstate ion, but the inflection in the pH titration curve is much sharper than with molybdate and is thus suitable for use analytically in the acidimetric titration of tungsten.

EXPERIMENTAL

Reagents

Standard sulphuric acid solutions, 1*N*, 0·1*N* and 0·01*N*.
Sodium hydroxide solutions, 1*M* and 0·1*M*.
Sodium tungstate solution, 0·100*M*.
Mannitol, laboratory reagent grade.

Titration curves

The titration of 25 ml of 0·1*M* sodium tungstate plus 50 ml of water (*a*) alone and (*b*) with 10 g of mannitol added was followed potentiometrically. In the absence of mannitol the curve had a shallow inflection corresponding to the addition of approximately 1·25 protons per tungstate ion, but in the presence of mannitol a sharp drop in pH occurred when exactly one proton per tungstate ion had been added. To use this pH change as the end-point in an acidimetric determination of tungstate it would be essential to have all the tungstate present initially as WO_4^{2-} ions, with no other base present. This can readily be achieved by adding a small excess of sodium hydroxide solution to the tungstate solution and titrating the excess with acid. Mannitol may then be added and the titration of tungstate completed. Figure 1 shows the pH curve for this titration. It is noteworthy that the two inflection points occur at the pH values corresponding to the colour changes of phenolphthalein and Methyl Red respectively.

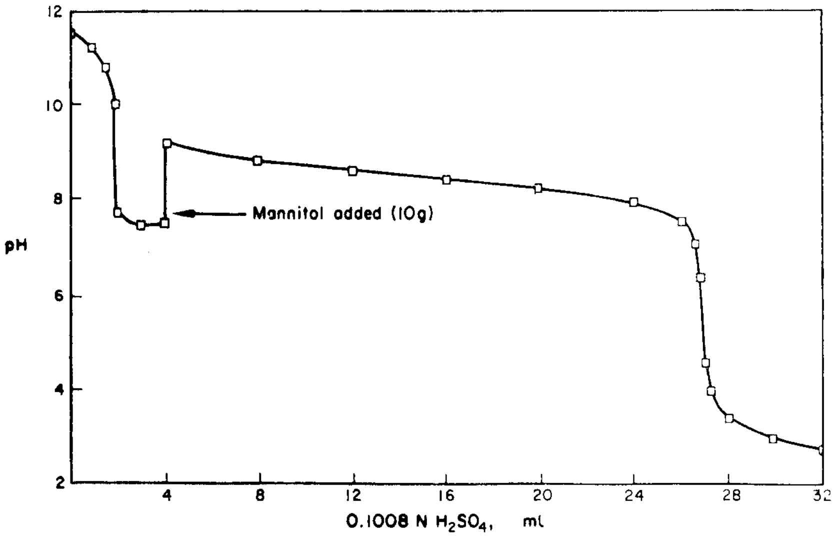

FIG. 1.—Typical pH curve for the titration of 0·2 mmole of NaOH plus 2·5 mmole of WO_4^{2-} in 50 ml of solution.

Analytical procedures

The basic analytical procedure is indicated above. At tungstate concentrations of 0·05*M* and above, phenolphthalein and Methyl Red may be used to detect the two equivalence points; both end-points are very sharp. At lower concentrations it is preferable to titrate to pH 8·5 and pH 5·5 respectively, using a pH meter. Since carbonate interferes, a blank titration on the reagents should always be carried out. Ammonia will also interfere, and if present in the sample should be removed by boiling with sodium hydroxide.

The nature and size of the sample for analysis will determine the details of the analytical procedure. For the determination of tungsten in alkali tungstates and tungstic oxide the following methods were found to be suitable.

Alkali tungstate salts. Dissolve 5·000 g of the sample in 100 ml of water in a 250-ml conical flask. Add one drop of the phenolphthalein indicator and make the solution alkaline with sodium hydroxide solution. Titrate carefully with 1·0*N* sulphuric acid until the pink colour disappears. Note the burette reading, add about 20 g of mannitol and 10 drops of Methyl Red indicator and continue the titration to the first appearance of a distinct pink colour. Calculate the tungsten present from the difference between the titrations, minus a blank titration on the same amounts of sodium hydroxide solution, mannitol and water, basing the calculation on the equation

$$x\mathrm{H}^+ + x\mathrm{WO_4}^{2-} + y\text{mannitol} = \text{complex.}$$

Tungstic oxide. Place 5·000 g of sample in a 250-ml perspex beaker containing a polythene-covered magnetic stirring bar. Add 60 ml of 1·0*M* sodium hydroxide, cover the beaker, and place it in a water-bath consisting of a 600-ml beaker heated on a combined hot-plate magnetic stirrer. Stirring for 15 min on the boiling water-bath is sufficient to dissolve all the tungstic oxide. Titrate with standard 1·0*N* sulphuric acid as described above. Carry out a blank titration on 60 ml of 1·0*M* sodium hydroxide treated as in the analysis of the sample. (Dissolution of tungstic oxide with alkali in glass beakers gives slightly high and variable results, presumably owing to silicate interference.)

Precision of the method

In titrations with 0·10*N* and 1·0*N* sulphuric acid both end-points are sharp to 0·01 ml. On five consecutive titrations of 25·00-ml portions of 0·100*M* sodium tungstate with 0·1008*N* acid the mean titre (after blank correction) was 24·86 ml and the relative standard deviation was 0·04%. Five analyses of a sample of AnalaR $\mathrm{Na_2WO_4{\cdot}2H_2O}$ gave a mean result of 55·9%W (theoretical value is 55·7%W) with a relative standard deviation of 0·10%. Five analyses of a sample of tungstic oxide gave a mean result of 78·9%W (78·8%W was found by oxine precipitation) and the relative standard deviation was again 0·10%. Finally, on five consecutive titrations of 25·00 ml of 0·0100*M* sodium tungstate solution with 0·01008*N* acid, in which the end-points were detected with a pH meter, the mean titre was 25·03 ml with a relative standard deviation of 0·48%.

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Summary—A new method is described for the acidimetric titration of tungstate, based on the reaction $x\mathrm{WO_4}^{2-} + x\mathrm{H}^+ + \text{mannitol} = \text{complex}$. Quantities of tungsten greater than 2·5 mmole may be determined with a relative standard deviation of not more than 0·1%. The method is subject to interference by any species in the tungstate solution which absorbs protons in the pH range 5·5–8·5.

Zusammenfassung—Ein neues Verfahren zur acidimetrischen Titration von Woflramat wird beschrieben, das auf der Reaktion

$$\mathrm{xWO_4}^{2-} + \mathrm{xH}^+ + \text{Mannit} = \text{Komplex}$$

beruht. Wolframmengen über 2,5 mMol können mit einer Standardabweichung von nicht mehr als 0,1% bestimmt werden. Die Methode ist störangällig gegenüber allen Spezies in der Wolframatlösung, die im pH-Bereich 5,5–8,5 Protonen aufnehmen.

Résumé—On décrit une nouvelle méthode pour le titrage acidimétrique du tungstate, basée sur la réaction: $x\mathrm{WO_4}^{2-} + x\mathrm{H}^+ + \text{mannitol} = \text{complexe}$. On peut doser des quantités de tungstène supérieures à 2,5 mmoles avec un écart type relatif non supérieur à 0,1%. La méthode est sujette à l'interférence de n'importe quelle espèce qui, dans la solution de tungstate, absorbe des protons dans le domaine de pH 5,5–8,5.

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Spectrophotometric determination of antimony with 3,5,7,4'-tetrahydroxyflavone (kaempferol)

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ANTIMONY and arsenic occur in small amounts in fission products in nuclear reactors. Antimony is also an important constituent of many lead alloys. Rhodamine-B,[1] potassium iodide,[1] Methyl Violet,[1] phenylfluorone,[2] sodium diethylthiocarbamate,[3] Alizarin Red-S[3] and thiourea[3] have been used for its spectrophotometric determination. Of these, the first two are widely used but suffer from interference by several ions.

In this communication investigations on kaempferol as a colorimetric reagent for determination of micro-amounts of antimony are reported.

EXPERIMENTAL

Reagents

Kaempferol was prepared by the method of Robinson and Sinoda.[4] A stock solution was prepared by dissolving a suitable amount in 95% methanol. Subsequent dilutions were made with 95% methanol.

Antimony(III) solution was prepared by dissolving the trichloride in 6*M* hydrochloric acid, and standardized gravimetrically. Subsequent dilutions were made with doubly distilled water when required.

All other reagents used were of reagent quality.

Reaction conditions

Absorption spectra of a series of solutions containing a fixed amount of antimony(III) and a 10-fold excess of ligand and different concentrations of hydrochloric acid were recorded against the corresponding reagent blanks (Fig. 1). The curves show an absorption maximum between 410 and 420 nm below pH 2·0, shifting to shorter wavelengths above this pH. The absorbance decreases as the concentration of hydrochloric acid is raised and decreases between pH 1 and 2. Above pH 2 it increases again and λ_{max} also shifts, pointing to formation of a new complex, probably by hydrolysis of the first. The complex exhibits practically constant and maximum absorption in the pH range 0·85–1·10. For further studies a wavelength of 420 nm and 0·1*M* hydrochloric acid medium were chosen.

Varying amounts of kaempferol were added to solutions containing fixed amounts (12·2 μg) of antimony. The solutions were made up to 10 ml in 0·1*M* hydrochloric acid and 40% methanol. A 10-fold molar excess of reagent is needed to give maximum absorbance.

The absorbance for fixed amounts of antimony and reagent increases in methanol concentration, but is constant between 35 and 45% v/v methanol, and then decreases again. Further studies were made in 40% v/v methanol medium. The complex is insoluble in 30% v/v methanol solution. The reaction is instantaneous and the colour is stable for 24 hr at near room temperature.

Beer's law is obeyed at 420 nm over the range up to 7·8 ppm of antimony. The molar absorptivity is $1{\cdot}09 \times 10^4$ and the accurate range of determination[5] 1·9–7·8 ppm of antimony.

Job's method[6] and the slope-ratio method[7] show that the combining ratio of antimony(III) and kaempferol in the complex is 1:1.

Recommended procedure

Take, in a 10-ml standard flask a suitable aliquot of sample solution containing 20–80 μg of antimony and add 2 ml of 0·1% methanolic reagent solution. Add 2 ml of methanol, dilute to volume, mix, and measure the absorbance at 420 nm against a reagent blank. The acidity should be 0·1*M*, in hydrochloric acid.

Interferences

Since the determination is carried out in 0·1*M* hydrochloric acid medium, ions which form chelates only at lower acidity values do not interfere. The tolerance limits (in brackets, in ppm) for rare earths and common ions with 4·8 ppm of antimony were found to be: Al(5·5), Be(60), Mg(150), Ca(400), Sr(400), Ba(100), Sc(9), Y(20), La(70), Er(84), Ce(140), Gd(80), Nd(72), Sm(75), Co(120), Ni(200), Cu(70), Zn(80), Cd(150), Hg(400), Ga(1·44), Tl(100), Pd(400), As(300), Se and Te(70).

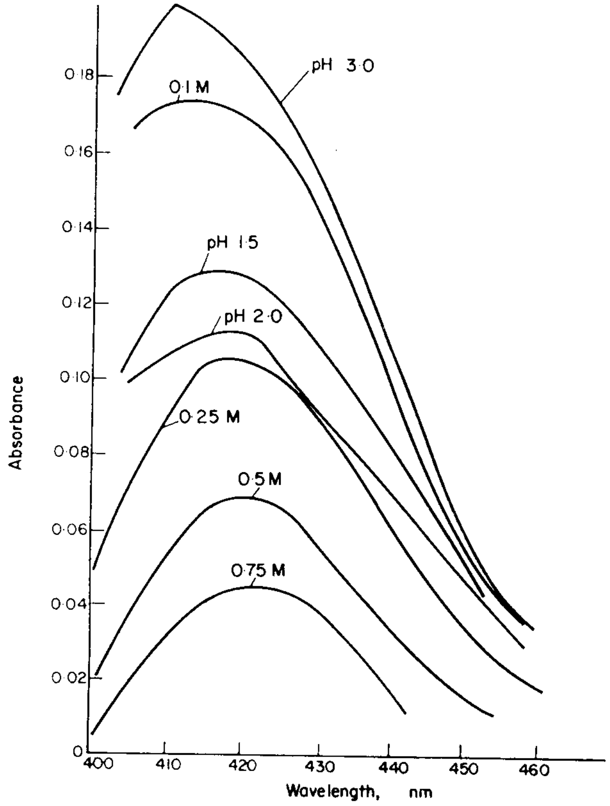

FIG. 1.—Absorption spectra of antimony–kaempferol complex at different hydrochloric acid concentrations.

Elements such as zirconium, titanium, tungsten, molybdenum and iron(III) interfere even when they are present in small quantities. Niobium and tantalum are precipitated under these conditions.

The tolerances (ppm) of some anions were found to be: SO_4^{2-}(380), ClO_4^-(2000), BO_3^{3-}(400), NO_3^-(900), $CH_3CO_2^-$(800), PO_4^{3-}(160), SO_3^{2-}(400), I^-(60), Br^-(800), IO_3^-(20), SCN^-(35). Fluoride, thiosulphate, ascorbic acid and EDTA interfere seriously.

Acknowledgement—Two of the authors (B. S. G.) and (K. C. T.) are thankful to the Council of Scientific and Industrial Research, Rafi Marg, New Delhi (India) for the award of fellowships.

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Summary—A selective spectrophotometric method is described for determination of antimony with kaempferol. Microgram amounts of antimony can be determined by measurements at 420 nm in 0·1*M* hydrochloric acid. The molar absorptivity is 1.09×10^4 at 420 nm and the optimum range for accurate determination is 1.9–7.8 ppm of antimony.

Zusammenfassung—Eine selektive spektrophotometrische Methode zur Bestimmung von Antimon mit Kaempferol wird beschrieben. Mikrogrammengen Antimon können durch Messung bei 420 nm in 0,1 M Salzsäure bestimmt werden. Der molare Extinktionskoeffizient beträgt $1{,}09 \cdot 10^4$ bei 420 nm und der optimale Bereich für genaue Bestimmung ist 1,9–7,8 ppm Antimon.

Résumé—On décrit une méthode spectrophotométrique sélective pour le dosage de l'antimoine avec le kampférol. On peut déterminer des quantités d'antimoine de l'ordre du microgramme par des mesures à 420 nm en acide chlorhydrique 0,1*M*. Le coefficient d'absorption moléculaire est 1,09 × 10^4 à 420 nm et le domaine optimal pour une détermination précise est de 1,9–7,8 ppm d'antimoine.

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Microdetermination of carbon and hydrogen*

Automatic combustion in a dynamic system

(*Received* 5 *March* 1968. *Accepted* 28 *July* 1968)

THE construction of an apparatus for the automatic microdetermination of carbon and hydrogen requires a reliable procedure for the automatic combustion of compounds varying widely in composition, structure and physical properties. For this purpose we made use of the principle of oxidation by excess of gaseous oxygen in the modification proposed by us 1,2 known as "wide tube combustion." This method avoids the formation of carbon slags which often accompany the combustion of organic compounds on the surface of an oxidizing agent in an inert gas atmosphere. An essential feature of our modification is that the combustion takes place with a turbulent flow of oxygen within a special container. At the same time direct contact with the rapidly passing stream of gas that could lead to loss of some of the sample is avoided.

The details of the method are as follows: the sample (5–10 mg) weighed in a boat (if solid) or in a glass or quartz capillary (if liquid) is placed in a cylindrical quartz container closed at one end. The whole is then introduced into a combustion tube (Fig. 1) through which a stream of oxygen is passed at the rate of 150–200 ml/min. If the sample contains interfering elements, suitable absorbent is placed in the container together with the sample, or in the combustion tube. The sample is burned by means of an electric heater moving in a direction opposite to that of the oxygen stream, beginning from the open end of the container; within 5 min the whole container has achieved the desired temperature (900–1000°). The heater remains for 3 min at the end of its travel, is returned rapidly to the standing position, where it remains for 3 min while the container cools, then moves to the container again and heats it for a 4-min period, and finally returns to the start, thus finishing the combustion cycle. The actual sample burning time required for complete combustion is a few seconds. Combustion occurs within the space bounded by the container walls on one side and a high temperature zone at the open end on the other. The rapid flow of oxygen provides for a stable excess of this gas in the combustion zone. Moreover the turbulent motion of the gas rapidly sweeps the combustion products out of the container without carrying away any unoxidized particles. The total time of the combustion, including preliminary purging of the combustion train and the final sweeping-out period, is 15 min.

This method of combustion is in many respects similar to the flask combustion method, but has certain advantages over it. In combustion in a flask sample vapour may leave the hot zone and

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* Presented at the XXIst IUPAC Congress, Prague, 1967.

TABLE I.—SOME VALUES OF STANDARD DEVIATION FOR AUTOMATIC COMBUSTION PROCEDURE

Type of compound	Elements present	Carbon, %	Hydrogen, %	Reagent in container	Number of determinations	s or s_g, % abs.	
						C	H
Carbon chain polymers	CH	90–93	6–8	none	10	0·15	0·01
Acetonitrile	CHN	58·5	7·4	none	10	0·20	0·15
Triphenylphosphine	CHP	82·4	5·8	none	10	0·19	0·13
Chlorosilanes, siloxanes, cyclosilazanes	CHSiCl, CHOSi, CHNSi	60–64	5–7	asbestos	10	0·10	0·08
Carboranes	CHB, CHBO, CHBN	34–44	6–9	none	10	0·19	0·06
Polyfluoroalkyls, fluorophosphine-oxides fluoroborates	CHF, CHOF, CHOFP, CHNBF	53–58	3–5	magnesium oxide on pumice	10	0·23	0·02
Carborane complexes with diphenylphosphine and metal halides	CHBPNHal	33–44	3–4		10	0·16	0·05
Carborane complexes with transition and alkali metals	CHBFeCs	8–11	4–5		10	0·30	0·12

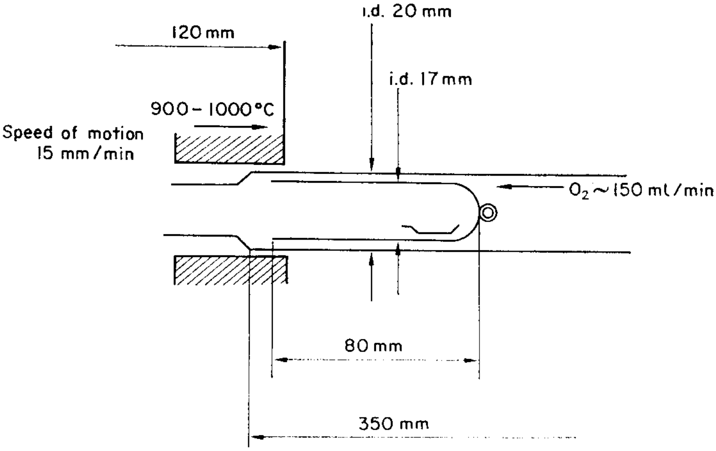

FIG. 1

impinge on the cold wall where oxidation is incomplete. In our procedure, because the whole container is heated, incomplete combustion is avoided. Our investigations have shown that the temperature and amount of oxygen are sufficient to ensure quantitative oxidation of milligram samples.

Long experience of this automatic combustion unit for the gravimetric determination of carbon and hydrogen shows it to possess considerable advantages over the manual pyrolytic method, including better reproducibility, the possibility of rapid quantitative oxidation of any organic or organo-metallic compounds, in particular those resistant to combustion, for instance carboranes, siloxanes, cyclosilazanes and other organo-silicon compounds, polymers with inorganic main chains, organo-fluorine or organo-phosphorus compounds *etc.*, and simplification of analysis of organo-fluorine and organo-silicon compounds, which are combusted in the presence of magnesium oxide or asbestos respectively (enough absorbent can be placed in the container to provide for 50–100 combustions; the analysis of such compounds then becomes as simple as that of those without hetero-elements). This automatic combustion device was tested on more than 3000 samples. Statistical treatment of the results (Table I) has shown the absolute error to be within the usual limits. Calculation of the standard deviation was made according to the formulae:

$$\text{Standard deviation } s = \sqrt{\frac{\Sigma e^2}{n-1}}\,.$$

$$\text{Pooled standard deviation } s_g = \sqrt{\frac{\Sigma e_1^2 + \Sigma e_2^2 + \ldots \Sigma e_g^2}{(n_1 + n_2 + \ldots n_g) - g}}\,.$$

The combustion method described has been used in the construction of a completely automated carbon–hydrogen analyser based on non-dispersive infrared carbon dioxide determination and the coulometric determination of water. Preliminary standard deviation data are satisfactory.

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Summary—An automatic combustion method has been developed for organic and organo-metallic compounds (5–10 mg samples), based on "wide tube" dynamic combustion in a turbulent oxygen atmosphere. Hydrocarbons, carboranes, transition metal carboran complexes, highly fluorinated compounds, silanes, siloxanes and cyclosilazanes, fluoro-derivatives of alkyl phosphinic acids, high polymers, *etc.* have been analysed by it. Silver-plated pumice, magnesium oxide, fibrous asbestos and crushed quartz were used to absorb interfering elements. Advantages over the manual procedure are simplicity of procedure, rapid combustion of difficultly combustible or highly volatile compounds, and better reproducibility of the results. The overall combustion cycle takes 15 min. The standard deviation for hydrogen is 0·01–0·15% and for carbon is 0·10–0·23% (carbon content 20–95%).

Zusammenfassung—Eine automatische Verbrennungsmethode für organische und metallorganische Verbindungen (Proben von 5–10 mg) wurde entwickelt. Sie beruht auf der dynamischen Verbrennung in einer turbulenten Sauerstoffatmosphäre. Kohlenwasserstoffe, Carborane, Carborankomplexe von Übergangsmetallen, hochfluorierte Verbindungen, Silane, Siloxane und Cyclosilazane, Fluorderivate von Alkylphosphinsäuren, Hochpolymere usw. wurden damit analysiert. Silber auf Bimsstein, Magnesiumoxid, faseriger Asbest und zerkleinerte Quartz wurden verwendet, um störende Elemente zu absorbieren. Vorteile gegenüber dem manuellen Verfahren sind die Einfachheit des Vorgehens, die schnelle Verbrennung schwer verbrennbarer oder stark flüchtiger Verbindungen und bessers Reproduzierbarkeit der Ergebnisse. Ein Verbrennungsvorgang dauert 15 Minuten. Die Standardabweichung für Wasserstoff ist 0,1–0,15% und für Kohlenstoff 0,10–0,23% (Kohlenstoffgehalt 20–95%).

Résumé—On a élaboré une méthode de combustion automatique pour les composés organiques et organo-métalliques (échantillons de 5–10 mg) basée sur la combustion dynamique dans une atmosphère d'oxygène turbulente. On a analysé par cette méthode des hydrocarbures, carboranes, complexes métal de transition carborane, composés hautement fluorés, silanes, siloxanes et cyclosilazanes, dérivés fluorés d'acides alkylphosphiniques, hauts polymères, etc... Pour absorber les éléments gênants, on a utilisé la ponce argentée, l'oxyde de magnésium, l'amiante fibreuse et le quartz broyé. Les avantages sur le mode opératoire manuel sont la simplicité de la technique, la combustion rapide de composés difficilement combustibles ou hautement volatils et une meilleure reproductibilité des résultats. L'ensemble du cycle de combustion nécessite 15 mn. L'écart type pour l'hydrogène est 0,01–0,15% et pour le carbone 0,10–0,23% (teneur en carbone 20–95%).

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LETTERS TO THE EDITOR

The use of aluminium capsules in the Perkin–Elmer CHN Analyzer

SIR,

In a paper by Culmo and Fyans,[1] the method recommended for the analysis of volatile samples which cannot be weighed in open containers is to seal the sample in an aluminium capsule which is weighed. The capsule is placed in a long-handled quartz "spoon" or "ladle", inserted into the quartz combustion tube and heated at 950°.

After using this method for a short time, we found that unless steps are taken to prevent it, pieces of aluminium oxide are ejected from the spoon and fuse into the wall of the combustion tube, eventually forming a crack or hole which causes spurious results to be obtained. One of our combustion tubes lasted only 3 days after continuous use with aluminium capsules.

We have now overcome this trouble by lining the bottom of the spoon with thin platinum foil, because the spoon is also attacked, and covering the capsule with fine platinum gauze. The platinum foil is attacked by the aluminium and has to be replaced after about 4 dozen capsules have been heated on it.

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17 *September* 1968

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The masking coefficient in precipitation reactions

SIR,

The modified equation by Ryan[1] is useful for calculation of the amount of chelating agent needed for complete masking. This modification is a more general form of the masking coefficient equation[2] used by Kelly and Sutton[3] to predict precipitation reactions. The pM′ values calculated from Ryan's equation, however, do not differ significantly from those reported by Kelly and Sutton in the region of nearly complete precipitation, and their results[3] are valid.

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Vanadium (II)–1,10-phenanthroline complex as a redox indicator

SIR,

Schaefer has suggested the use of the chelate complex formed between vanadium(II) ions and 1,10-phenanthroline as an indicator for use with the strongly reducing titrant chromium(II).[1] The indicator, which has a deep blue-violet reduced form ($\lambda_{max} = 645$ nm; $\varepsilon = 8000$ l. mole^{-1}. cm^{-1}) and an almost colourless oxidized form, possesses a formal potential of about +0·2 V; hence its usefulness in conjunction with the Cr(III)–Cr(II) couple ($E^\circ = -0{\cdot}41$ V). The indicator compares very favourably with various dyes and diphenylamine derivatives of colourless reduced form proposed by Tandon and Mehrotra for the same titration.[2]

Schaefer applied his indicator only to the titration of iron(III) in order to demonstrate its likely utility. We have extended the use of the indicator to the micro-scale determination of KIO_3, $KBrO_3$, $KClO_3$, $NaNO_3$, and the nitro-compounds listed below. The colour change is rapid and fully rereversible at room temperature. The intensely coloured reduced form competes well with the green background colour from Cr(III).

Bromate and iodate may be titrated directly with Cr(II) under the conditions described by Schaefer for Fe(III). Aromatic nitro-compounds (picric acid; 2-nitrodiphenylamine; 2,4-dinitrotoluene; 2,4,6-trinitrotoluene) and chlorate were determined by a back-titration with Fe(III) following treatment with excess of Cr(II). A 60% ethanol solution was used for the nitro-compound work. Nitrate and nitroglycerine were determined in similar manner but the addition of Fe(III) and Ti(IV) to form effective reaction intermediates, as suggested by Lingane,[3] was found necessary.

Recoveries on approximately 1 mg samples were very good, the precision being indicated by a mean coefficient of variation of 0·92%.

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7 August 1968

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NOTE

SI UNITS*

SI (which is the abbreviation in many languages for Système International d'Unités) is an extension and refinement of the traditional metric system. It embodies features which make it logically superior to any other system as well as practically more convenient: it is rational, coherent, and comprehensive.

Over the years much thought has been given to extending and improving the metric system until finally in 1960 the Conférence Générale des Poids et Mesures, the body responsible for maintaining standards of measurements, formally approved SI. Already nearly thirty countries have decided to make it the only legally accepted system and it is clearly destined to become the universal currency of science and commerce.

The main features of SI are as follows:

1. There are six basic units (see below), the metre and kilogramme taking the place of the centimetre and gramme of the old metric system.
2. The unit of force, the newton (kg m s^{-2}), is independent of the Earth's gravitation, and the often confusing introduction, in some branches of science and technology, of g into equations is no longer necessary.
3. The unit of energy in all forms is the joule (newton × metre), and the unit of power is the joule per second (watt); thus the variously defined calories, together with the kilowatt hour, the B.t.u., and the horsepower are all superseded.
4. 'Electrostatic' and 'electromagnetic' units are replaced by SI electrical units.
5. Multiples of units are normally to be restricted to steps of a thousand and similarly fractions to steps of a thousandth.

Lists are appended of the basic SI units, of some derived SI units, of compatible units, and also examples of units which run counter to SI, the use of which is accordingly to be actively discouraged. Also listed are the names and symbols of the prefixes representing numerical factors: these are both convenient in obviating the need to write large numbers of zeros or in some instances high powers of 10, and also helpful in establishing familiarity with the numerical framework of modern science. It will be noted that the recommended prefixes are limited to $10^{\pm 3n}$.

BASIC SI UNITS

physical quantity	*name of unit*	*symbol for unit*
length	metre	m
mass	kilogramme	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	degree Kelvin	°K
luminous intensity	candela	cd

Symbols for units do not take a plural form.

SUPPLEMENTARY UNITS

These units are dimensionless.

physical quantity	*name of unit*	*symbol for unit*
plane angle	radian	rad
solid angle	steradian	sr

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* Abstracted from *Metrication in Scientific Journals*, Royal Society, London, 1968, by permission.

DERIVED SI UNITS WITH SPECIAL NAMES

physical quantity	*name of unit*	*symbol for unit*	*definition of unit*
energy	joule	J	$\mathrm{kg\ m^2\ s^{-2}}$
force	newton	N	$\mathrm{kg\ m\ s^{-2} = J\ m^{-1}}$
power	watt	W	$\mathrm{kg\ m^2\ s^{-3} = J\ s^{-1}}$
electric charge	coulomb	C	A s
electric potential difference	volt	V	$\mathrm{kg\ m^2\ s^{-3}\ A^{-1} = J\ A^{-1}\ s^{-1}}$
electric resistance	ohm	Ω	$\mathrm{kg\ m^2\ s^{-3}\ A^{-2} = V\ A^{-1}}$
electric capacitance	farad	F	$\mathrm{A^2\ s^4\ kg^{-1}\ m^{-2} = A\ s\ V^{-1}}$
magnetic flux	weber	Wb	$\mathrm{kg\ m^2\ s^{-2}\ A^{-1} = V\ s}$
inductance	henry	H	$\mathrm{kg\ m^2\ s^{-2}\ A^{-2} = V\ s\ A^{-1}}$
magnetic flux density	tesla	T	$\mathrm{kg\ s^{-2}\ A^{-1} = V\ s\ m^{-2}}$
luminous flux	lumen	lm	cd sr
illumination	lux	lx	$\mathrm{cd\ sr\ m^{-2}}$
frequency	hertz	Hz	cycle per second
customary temperature, t	degree Celsius	°C	$t/°\mathrm{C} = T/°\mathrm{K} - 273{\cdot}15$

FRACTIONS AND MULTIPLES

fraction	*prefix*	*symbol*	*multiple*	*prefix*	*symbol*	
10^{-1}	deci	d	10	deka	da	
10^{-2}	centi	c	10^2	hecto	h	†
10^{-3}	milli	m	10^3	kilo	k	
10^{-6}	micro	μ	10^6	mega	M	
10^{-9}	nano	n	10^9	giga	G	
10^{-12}	pico	p	10^{12}	tera	T	
10^{-15}	femto	f				
10^{-18}	atto	a				

† To be restricted to instances where there is a strongly felt need, such as may be experienced in the early days of metrication in favour of the centimetre as the unit of length in certain biological measurements.

Compound prefixes should not be used, e.g. 10^{-9} metre is represented by

1 nm, ***not*** 1 mμm.

The attaching of a prefix to a unit in effect constitutes a new unit, e.g.

$$1\ \mathrm{km^2} = 1\ \mathrm{(km)^2} = 10^6\mathrm{m^2}$$
$$\textit{not}\ 1\ \mathrm{k(m^2)} = 10^3\mathrm{m^2}.$$

Where possible any numerical prefix should appear in the numerator of an expression.

EXAMPLES OF OTHER DERIVED SI UNITS

physical quantity	*I unit*	*symbol for unit*
area	square metre	$\mathrm{m^2}$
volume	cubic metre	$\mathrm{m^3}$
density	kilogramme per cubic metre	$\mathrm{kg\ m^{-3}}$
velocity	metre per second	$\mathrm{m\ s^{-1}}$
angular velocity	radian per second	$\mathrm{rad\ s^{-1}}$
acceleration	metre per second squared	$\mathrm{m\ s^{-2}}$
pressure	newton per squared metre	$\mathrm{N\ m^{-2}}$
kinematic viscosity, diffusion coefficient	square metre per second	$\mathrm{m^2\ s^{-1}}$
dynamic viscosity	newton second per square metre	$\mathrm{N\ s\ m^{-2}}$
electric field strength	volt per metre	$\mathrm{V\ m^{-1}}$
magnetic field strength	ampere per metre	$\mathrm{A\ m^{-1}}$
luminance	candela per square metre	$\mathrm{cd\ m^{-2}}$

UNITS TO BE ALLOWED IN CONJUNCTION WITH SI

physical quantity	*name of unit*	*symbol for unit*	*definition of unit*
length	parsec	pc	30·87 × 10^{15} m
area	barn	b	10^{-28} m^2
	hectare	ha	10^4 m^2
volume	litre	l	10^{-3} $\mathrm{m}^3 = \mathrm{dm}^3$
pressure	bar	bar	10^5 N m^{-2}
mass	tonne	t	10^3 kg = Mg
kinematic viscosity, diffusion coefficient	stokes	St	10^{-4} $\mathrm{m}^2\,\mathrm{s}^{-1}$
dynamic viscosity	poise	P	10^{-1} kg $\mathrm{m}^{-1}\,\mathrm{s}^{-1}$
magnetic flux density (magnetic induction)	gauss	G	10^{-4} T
radioactivity	curie	Ci	37 × 10^9 s^{-1}
energy	electronvolt	eV	1·6021 × 10^{-19} J

The common units of time (e.g. hour, year) will persist, and also, in appropriate contexts, the angular degree.

Until such time as a new name may be adopted for the kilogramme as the basic unit of mass, the gramme will often be used, both as an elementary unit (to avoid the absurdity of mkg) and in association with numerical prefixes, e.g. μg.

EXAMPLES OF UNITS CONTRARY TO SI, WITH THEIR EQUIVALENTS

physical quantity	*unit*	*equivalent*
length	ångström	10^{-10} m
	inch	0·0254 m
	foot	0·3048 m
	yard	0·9144 m
	mile	1·60934 km
	nautical mile	1·85318 km
area	square inch	645·16 mm^2
	square foot	0.092903 m^2
	square yard	0·836127 m^2
	square mile	2·58999 km^2
volume	cubic inch	1·63871 × 10^{-5} m^3
	cubic foot	0·028316 8 m^3
	U.K. gallon	0·004546092 m^3
mass	pound	0·45359237 kg
	slug	14.5939 kg
density	pound/cubic inch	2·76799 × 10^4 kg m^{-3}
	pound/cubic foot	16.0185 kg m^{-3}
force	dyne	10^{-5} N
	poundal	0·138255 N
	pound-force	4·44822 N
	kilogramme-force	9·80665 N
pressure	atmosphere	101·325 kN m^{-2}
	torr	133·322 N m^{-2}
	pound (f)/sq.in.	6894·76 N m^{-2}
energy	erg	10^{-7} J
	calorie (I.T.)	4·1868 J
	calorie (15°C)	4·1855 J
	calorie (thermochemical)	4·184 J
	B.t.u.	1055·06 J
	foot poundal	0·042 140 1 J
	foot pound (f)	1·355 82 J
power	horse power	745·700 W
temperature	degree Rankine	$\frac{5}{9}$ °K
	degree Fahrenheit	$t/{}^\circ\mathrm{F} = \frac{9}{5}T/{}^\circ\mathrm{C} + 32$

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NOTICES

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

DIVISION OF ANALYTICAL CHEMISTRY COMMISSION ON MICROCHEMICAL TECHNIQUES AND TRACE ANALYSIS

The Commission intends to carry out a comparative collective study on microanalytical methods of C—H determination in organometallic compounds. The first stage is to collect information on analytical methods used and their advantages. The second stage of the work is to analyse a series of pure substances. Participants wishing to study only those classes of organometallic compound with which they work routinely, would play a limited part in this stage.

Reports, in English or Russian, should be addressed to: Dr. N. E. GEL'MAN, Institute for Elemental Organic Compounds, Academy of Sciences, Vavilova, 28, Moscow V-312, USSR. The deadline for this material will be 1 April 1969.

Information required on carbon-hydrogen determination in organometallic chemistry.

I. Compounds analysed, type, structure, essential properties.
II. Methods used for C—H determination.

Description of the method or a reprint should be enclosed. The following essential information must be given.

1. Sample size.
2. Standard deviation of the balance-readings, or the error of other procedures of sample measuring.
3. Mode of combustion (oxidation) and degree of automation.
   - (*a*) Whether static or dynamic procedure.
   - (*b*) Oxidizing reagents and catalysts (gaseous oxygen only, gaseous oxygen with addition of oxidants and catalysts, oxidants in inert atmosphere, *etc*).
   - (*c*) Temperatures of the main zones in combustion unit (evaporation, combustion, oxidative, absorption and other zones).
   - (*d*) Transport gas velocity, pressure and other possible critical factors.
   - (*e*) Duration of the actual combustion (oxidation) and of the whole analysis.
4. Chemical forms of C and H obtained for measuring.
5. Methods of measuring the end products (gravimetric, instrumental, *etc*); degree of automation.
6. Apparatus used (general description). Main principles and most important features. Combustion unit and measuring system.
7. Specific features of the analytical procedure for the types or organo-metallic compounds discussed.
   - (*a*) Types of compounds which can be analyzed by standard method.
   - (*b*) Interfering action of heteroelements and their volatile and non-volatile compounds.
   - (*c*) Elimination of interferences. General and particular recommendations.
   - (*d*) The number of combustions carried out without rearrangement of the unit.
   - (*e*) Analysis of unstable substances. Possibilities and limitations.
   - (*f*) Simultaneous determination of C, H and heteroelements in the same sample. Possibilities and limitations.
8. Accuracy and precision of analysis (if possible). Standard deviation for organic and organometallic compounds (at least 10 variates).
9. Summary and author's recommendations.

MEETINGS OF THE GESELLSCHAFT DEUTSCHER CHEMIKER IN 1969

10–15 March 1969	Symposium on Mass Spectrometry, and Atomic and Molecular Impact Processes, Heidelberg.
8–12 April 1969	Meeting on Analytical Chemistry.
15–18 April 1969	3rd International Protactinium Conference, Schloß Elmau, near Mittenwald (the number of participants is limited to 100).
22–26 April 1969	EUCHEM Conference "Metal Proteids," Isle of Heligoland (the number of participants is limited to 100 persons).
7–10 May 1969	Meeting of the Division for Coatings and Pigments, Bad Ems.
13–14 May 1969	Annual Meeting of the Division for Water Chemistry, Bad Dürrheim (Black Forest).
15–20 September 1969	General Assembly of the Gesellschaft Deutscher Chemiker, in Hamburg.
6–8 October 1969	Meeting of the Division of Applied Electrochemistry, on Organic Electrosynthesis, Bonn.

Details may be obtained from Gesellschaft Deutscher Chemiker, 6000 Frankfurt (M), Postfach 119075, Germany.

Talanta, 1969, Vol. 16, pp. vii to viii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Coulometrische Bestimmung von Chloraten: Peter Gründler and Heinz Holzapfel. (19 *November* 1968)

Rapid spectrophotometric determination of copper in steel with zinc dibenzyldithiocarbamate (ZDBDT): Om P. Bhargava. (12 *December* 1968)

Potentiometric determination of successive stability constants of ethylenediamine complexes of several metals in dimethylsulphoxide: Karl H. Pool and Donald E. Sandberg. (12 *December* 1968)

Studies on chelates of selected pyrazylmethyl ketones: John S. England and John C. Guyon. (13 *December* 1968)

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Reversed-phase partition chromatographic separations using mono- and bis-2-ethylhexyl phosphoric acids: S. J. Lyle and V. C. Nair. (16 *December* 1968)

Spectrophotometric determination of ruthenium using 8-quinolinol: Hiroshi Hashitani, Kazuo Katsuyama and Kenju Motojima. (18 *December* 1968)

Applications of enzyme-catalysed reactions in trace analysis—IV. Determination of beryllium and zinc by their inhibition of calf-intestinal alkaline phosphates: A. Townshend and A. Vaughan. (23 *December* 1968)

Applications of digital computers in analytical chemistry—I: C. W. Childs, P. S. Hallman and D. D. Perrin. (30 *December* 1968)

Applications of digital computers in analytical chemistry—II: C. W. Childs, P. S. Hallman and D. D. Perrin. (30 *December* 1968)

Properties of Calcein as an acid and as a fluorometric chelating agent for calcium: Alta J. Hefley and Harvey Diehl. (30 *December* 1968)

A general method for the determination of organic nitrogen by the application of the bromate and permanganate oxidants: M. A. Siddiqui, M. K. Bhatty and Muhammad Ashraf. (6 *January* 1969)

A Review of the methods of determining carbon dioxide: D. H. Davies. (6 *January* 1969)

Polarographic determination of aluminium with Alizarin: M. Kapel and D. W. Selby. (6 *January* 1969)

Determination of trace amounts of antimony in hydrobromic acid medium by inorganic spectrofluorimetry at liquid nitrogen temperature: G. F. Kirkbright, C. G. Saw, J. V. Thompson and T. S. West. (6 *January* 1969)

Kinetische Bestimmung von Molybdän unter Verwendung eines Potentiostaten: H. Weisz, D. Klockow and M. Ludwig. (6 *January* 1969)

A semiquantitative determination of ajmaline using Weisz ring-oven technique: R. A. Shah and Nargis Hussain. (6 January 1969)

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Assay of some organic bases in pharmaceutical preparations: I. M. Roushdi, S. A. Soliman and Y. A. Belgaty. (7 *January* 1969)

A new method for the assay of glutethimide: I. M. Roushdi, S. A. Soliman and Y. A. Belgaty. (7 *January* 1969)

The acidity of several chromotropic acid azo derivatives: B. BUDĚŠINSKÝ. (7 January 1969)

Separation of tervalent rare earths plus Sc from Al, Fe(III), Ti(IV) and other elements by cation-exchange chromatography in hydrochloric acid-ethanol: F. W. E. STRELOW and CYNTHIA BAXTER. (8 *January* 1969)

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Substituted phenothiazines as indicators in the titration of zinc with ferrocyanide: H. SANKE GOWDA and B. KESAVAN. (13 *January* 1969)

Determination of $Fe_2(CN)_6^{4-}$ with $Mo(CN)_8^{3-}$ electrolytically generated: J. HERNANDES MENDEZ and F. LUCENA CONDE. (13 *January* 1969)

Co-precipitation, kinetic and mechanistic aspects of the formation of nickel(II) and palladium(II) dimethylglyoximates from homogeneous solution containing biacetyl monoxime and hydrolylamine: S. J. LYLE and R. MAGHZIAN. (13 *January* 1969)

Precipitation and co-precipitation studies of dimethylglyoximates from metal ions, biacetyl and hydroxylamine: S. J. LYLE and R. MAGHZIAN. (13 *January* 1969)

The performance-characteristics of analytical methods—II: Precision: A. L. WILSON. (13 *January* 1969)

Film polarography: KH. Z. BRAININA. (13 *January* 1969)

Anion-exchange behaviour of several elements in hydrobromic acid–organic solvent media: E. KLAKL and J. KORKISCH. (13 January 1969)

Solid-liquid separation after liquid-liquid extraction: TAITIRO FUJINAGA, TORU KUWAMOTO and EIICHIRO NAKAYAMA. (14 *January* 1969)

A critical study of carminic acid as a reagent for the spectrophotometric determination of boron: H. K. L. GUPTA and D. F. BOLTZ. (14 *January* 1969)

Standardization of dilute ferrous solutions using a thermometric titration procedure: REED M. IZATT, H. DEE JOHNSTON, JOSEPH W. RICHARDS and JAMES J. CHRISTENSEN. (14 *January* 1969)

Spectrophotometric determination of palladium in titanium-base alloys with dimethylglyoxime: WARREN F. DAVIS. (14 *January* 1969)

Contribution to limits of detection in electron probe microanalysis: H. MALISSA and H. CHR. HORN. (16 *January* 1969)

Electrometric estimation of tripotassium aquotrihydroxotetracyanomolybdate(IV) and tetrapotassium tetrahydroxotetracyanotungstate(IV): KABIR-UD-DIN, A. A. KHAN and M. A. BEG. (16 *January* 1969)

Determination of nitrite and bromate with antipyrine and specific detection of bromate ions: MOHSIN QURESHI, NIGHAT ZEHRA and SUDARSHAN KUMAR. (16 *January* 1969)

Analytical applications of co-ordination compounds: J. N. BRAZIER. (17 *January* 1969)

Infrared emission from organic compounds stimulated by a laser beam: J. W. ROBINSON, D. M. HAILEY and H. M. BARNES. (17 *January* 1969)

Structure–activity relationships of some 5-nitro-2-furaldehyde oximes and hydrazones: G. A. HOWARTH, W. HOYLE and B. J. WAKEFIELD. (17 *January* 1969)

Direct determination of oxygen in organic materials—I. A study of the carbon reduction method: G. INGRAM and J. R. MAJER. (17 *January* 1969)

Effect of pH on concentration of species present in aqueous solutions of carbonyl compounds affected by hydration–dehydration and keto–enol equilibria: D. BARNES and P. ZUMAN. (20 *January* 1969)

Adsorption and displacement effects in the gas-chromatography of metal β-diketonates: P. C. UDEN and C. R. JENKINS. (21 *January* 1969)

SUMMARIES FOR CARD INDEXES

Polarography and physical chemistry of *N*-oxides—I. Reduction mechanism and hydration of the formylpyridine *N*-oxydes: E. Laviron and R. Gavasso, *Talanta*, 1969, **16**, 293. (Laboratoire de Polarographie Organique associé au C.N.R.S., Faculte des Sciences, Dijon, France.)

Summary—The 2-and 4-formylpyridine *N*-oxides show, in acid medium, an abnormal reduction mechanism. The first wave, with a potential which lies in the neighbourhood of the usual value for the aldehyde group, is due to the simultaneous reduction of the *N*-oxide group and the carbonyl group. The second wave is due to the reduction of the *N*-oxide group in the presence of a hydrated aldehyde group. 3-Formylpyridine *N*-oxide is reduced normally at all pH values, with the reduction of the carbonyl group preceding that of the *N*-oxide group. The reduction mechanisms have been verified by controlled potential electrolysis. The hydration of the carbonyl group has been studied by polarographic and spectrophotometric methods.

A chemical concentration X-ray determination of selenium in copper-, nickel- and iron-base alloys: C. H. Albright, Keith E. Burke and M. M. Yanak, *Talanta*, 1969, **16**, 309. (International Nickel Company, Inc., Paul D. Merica Research Laboratory, Sterling Forest, Suffern, New York 10901, U.S.A.)

Summary—A method is described for the determination of selenium in various metals and alloys at concentrations of 3–100 ppm. A chemical separation is made by filtration after reduction of the selenious acid to elemental selenium with hydroxylamine hydrochloride. The pure selenium product is readily analysed by X-ray fluorescence; the method is free from errors due to matrix effects. The relative standard deviation is 6% for a copper–nickel alloy at the 60 ppm level.

ИЗУЧЕНИЕ *N*-ОКИСЕЙ ПОЛЯРОГРАФИЧЕСКИМ И ФИЗИКО-ХИМИЧЕСКИМ МЕТОДАМИ—I. МЕХАНИЗМ ВОССТАНОВЛЕНИЯ И ГИДРАТАЦИИ *N*-ОКИСЕЙ ФОРМИЛПИРИДНОВ:

E. Laviron and R. Gavasso, *Talanta*, 1969, **16**, 293.

Резюме—В кислой среде *N*-окиси 2- и 4-формилпиридинов показывают ненормальный механизм восстановления. Первая волна, потенциал которой в соседству обыкновенной величины для альдегидной группы, вызвана одновременным восстановлением *N*-окиси и карбонильной группы. Вторая волна вызвана восстановлением *N*-окиси в присутствии гидратизированной альдегидной группы. *N*-окись 3-формилпиридина восстанавливается нормально во всех областях pH, а восстановление карбонильной группы предшествует восстановлению *N*-окиси. Механизмы восстановления подтверждены методом электролиза при контроллированномпотенциале. Гидратация карбонильной группы изучена полярографическим и спектрофотометрическим методами.

ОПРЕДЕЛЕНИЕ СЕЛЕНА В СПЛАВАХ НА ОСНОВЕ МЕДИ, НИКЕЛЯ И ЖЕЛЕЗА МЕТОДОМ РЕНТГЕНОВСКОЙ СПЕКТРОСКОПИИ ПОСЛЕ КОНЦЕНТРИРОВАНИЯ ХИМИЧЕСКИМ ПУТЕМ:

C. H. Albright, Keith E. Burke and M. M. Yanak, *Talanta*, 1969, **16**, 309.

Резюме—Описан метод определения селена в разных металлах и сплавах при концентрациях 3–100 мкг/г. Выделение получено фильтрованием после восстановления селенистой кислоты в элементарный селен хлористоводородным гидроксиламином. Полученный чистый селен легко анализируется методом рентгеновской флуоресценции. Метод не подлежает ошибкам на основе матричных эффектов. Относительная стандартная ошибка 6% при 60 мкг/г для сплава меди и никеля.

Germanomolybdic acid and its reaction with basic organic dyestuffs—I. Spectrophotometric determination of Ge(IV) with xanthene dyes: Gr. Popa and I. Paralescu, *Talanta*, 1969, **16,** 315. (Faculty of Chemistry, University of Bucharest, Spl. Independentei 89, Bucharest, Rumania.)

Summary—The interaction between germanomolybdic acid and four xanthene dyes (Rhodamine B, Rhodamine 6G, Rhodamine S and Pyronine G) is studied and the conditions for spectrophotometric determination of Ge(IV) with these reagents are established.

Collection of traces of metals on carboxy cellulose cation-exchanger: E. Schulek†, Zs. Remport-Horváth, A. Lásztity and E. Körös, *Talanta*, 1969, **16,** 323. (Institute of Inorganic and Analytical Chemistry, Eötvös Lóránd University, Budapest, Hungary.)

Summary—Carboxy cellulose ("C-cell") is a cation-exchanger based on cellulose and having carboxyl functional groups with p*K* 3·46 ± 0·05 at 20 ± 1° in 1*M* sodium chloride. The capacity of the exchanger is pH-dependent and the maximum is 0·22 mequiv/g. The capacity is also influenced by the dielectric constant of the medium and by the swelling of the cellulose. C-cell is suitable for the collection of metal ion impurities from aqueous and non-aqueous media.

Eléments de fluorimétrie organique fonctionnelle—II: M. Pesez and J. Bartos, *Talanta*, 1969, **16,** 331. (Centre de Recherches Roussel-Uclaf, 93-Romainville, France.)

Summary—α-Amino acids are converted into fluorescent derivatives of dihydrolutidine. Primary and secondary alkylamines are determined by converting them into sulphonamides by means of 1-dimethylaminonaphthalene-5-sulphonyl chloride. A fluorescent adduct is given by the reaction of tertiary alkylamines with α,γ-anhydroaconitic acid in acetic anhydride, and a fluorescence is obtained by condensing indoles with formaldehyde in the presence of an oxidizing agent. Furfural, obtained by the dehydration of pentoses, is determined by converting it into a 1,8-dioxodecahydroacridine derivative. 2,6-Di-t-butyl-*p*-cresol allows the fluorimetry of Δ^4 and $\Delta^{1,4}$-3,11-diketosteroids. The fluorescence of Pyronine G decreases under the action of $\Delta^{5(10)}$-3-keto-19-norsteroids.

ГЕРМАНОМОЛИБДЕНОВАЯ КИСЛОТА И ЕЕ РЕАКЦИЯ С ОСНОВНЫМИ ОРГАНИЧЕСКИМИ КРАСИТЕЛЯМИ:—I. СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ Ge(IV) С КСАНТЕНОВЫМИ КРАСИТЕЛЯМИ:

Gr. Popa and I. Paralescu, *Talanta*, 1969, **16**, 315.

Резюме—Изучено взаимодействие между германомолибденовой кислотой и четыре ксантеновых красителями (родамин B, родамин 6G, родамин S и пиронин G) и определены условия для спектрофотометрического определения Ge(IV) этими реагентами.

СОБИРАНИЕ СЛЕДОВ МЕТАЛЛОВ НА КАРБОКСИЦЕЛЛЮЛОЗНОМ ИОНООБМЕННИКЕ:

E. Schulek†, Zs. Remport-Horváth, A. Lásztity and E. Körös, *Talanta*, 1969, **16**, 323.

Резюме—Карбоксицеллюлоза ("C-cell") представляет собой катионообменник основывающийся на целлюлозе и содержающий карбоксильные функциональные группы с рK 3,46 ± 0,05 при 20 ± 1° в IM хлориде натрия. Ёмкость обменника зависит от рН-максимальная величина 0,22 меквив./г. Диэлектрическая константа среды и набухание целлюлозы также влияют на ёмкость. C-cell ом можно пользоваться для собирания следов ионов металлов из водных и неводных средах.

ОСНОВЫ ОРГАНИЧЕСКОЙ ФУНКЦИОНАЛЬНОЙ ФЛУОРИМЕТРИИ II:

M. Pesez and J. Bartos, *Talanta*, 1969, **16**, 331.

Резюме—Альфа-аминокислоты превращают в флуоресцирующие производные дигидролутидина. Первичные и вторичные алкиламины определяют превращением в сульфонамиды с использованием 1-диметиламинонафталин-5-сульфонилхлорида. Флуоресцирующий комплеск образуется в реакции третичных алкиламинов с α, γ-ангилроаконитовой кислотой в ангидриде уксусной кислоты, а флуоресцирующий продукт получается в конденсации индолов с формальдегидом в присутствии окисляющего агента. Полученный дегидратацией пентоз фурфурал определяют его превращением в дериват 1,8-диоксодекагидроакридина. 2,6-Ди-терт-бутил-п-крезол позволяет флуориметрию Δ^4 и $\Delta^{1,4}$-3, II-дикетостероидов. Флуоресценция пиронина Г уменьшается под действием $\Delta^{5(10)}$-3-кето-19-норстероидов.

Radiochemical microdetermination of manganese, strontium and barium by ion-exchange: Isidore Hadzistelios and Catherine Papadopoulou, *Talanta*, 1969, **16**, 337. (Nuclear Research Center "Democritos" Agia Paraskevi Attikis, Athens, Greece.)

Summary—A rapid radiochemical ion-exchange method has been developed for the quantitative separation of microamounts of Mn, Sr and Ba in the presence of other elements with atomic numbers below 84. The method proposed, combined with neutron-activation analysis, has been successfully applied to the simultaneous determination of Mn, Sr and Ba in plant and animal tissues. The method is simple and accurate.

Analysis of isotopic radium in thorium mill effluents: V. A. Kamath and P. P. Parekh, *Talanta*, 1969, **16**, 345. (Analytical Division, Bhabha Atomic Research Centre, Trombay, Bombay-74, India.)

Summary—A simple and rapid method has been developed for the determination of isotopic radium, based on γ-ray spectrometry. ^{228}Ra and ^{224}Ra are assayed by measuring the intensities of the photo-peaks in the 0·94 and the 2·62 MeV regions of the γ-spectrum. The interference in these measurements, arising from the presence of the ^{226}Ra–^{210}Pb chain in the sample, is obviated by the almost complete expulsion of ^{222}Rn from the system. The precision of the method is ±2% and ±3% in the determination of ^{228}Ra and ^{224}Ra respectively, the absolute sensitivities being 2 and 0·5 nCi. The method has been applied to evaluate the distribution of these isotopes in the various products of the Indian Rare-Earths Factory, Alwaye.

Anwendung der Röntgenfluoreszenz in der Supurenanalyse—II. Anreicherung von Spurenmetallen durch Fällung mit 1-(2-Pyridylazo)-2-naphthol: Richard Püschel, *Talanta*, 1969, **16**, 351. (Versuchsanstalt, Metallwerk Plansee AG., A-6600 Reutte, Austria.)

Summary—Up to 100 μg each of manganese, iron, cobalt, nickel, copper and zinc are precipitated at pH 10 by the addition of an alcoholic solution of PAN. The precipitate is collected on a filter paper, dried, and the elements determined directly by X-ray fluorescence measurements. The sensitivity, accuracy and reproducibility are reported for each element. As little as 0.1–0.5 μg of each may be determined in 50 ml of solution.

РАДИОХИМИЧЕСКОЕ МИКРООПРЕДЕЛЕНИЕ МАРГАНЦА, СТРОНЦИЯ И БАРИЯ С ПРИМЕНЕНИЕМ ИОННОГО ОБМЕНА:

ISIDORE HADZISTELIOS and CATHERINE PAPADOPOULOU, *Talanta*, 1969, **16**, 337.

Резюме—Разработан быстрый ионообменно-радиохимический метод для количественного выделения микроколичеств Mn, Sr, и Ba в присутствии других элементов с атомным числом ниже 84. Предложенным методом успешно пользовались—вместе с нейтронно—активационным анализом—для одновременного определения Mn, Sr, и Ba в растительных и животных тканях. Метод является несложным и точным.

ОПРЕДЕЛЕНИЕ ИЗОТОПОВ РАДИЯ В СТОЧНЫХ ВОДАХ ФАБРИКИ ТОРИЯ:

V. A. KAMATH and P. P. PAREKH, Talanta 1969, **16**, 345.

Резюме—Разработан несложный и быстрый метод определения изотопов радия методом спектрометрии гамма лучей. ^{228}Ra и ^{224}Ra анализировали измерением интенсивности фотопиков в областях 0,94 и 2,62 мэв гамма спектра. Влияние цепи ^{226}Ra–^{210}Pb в пробе избегнуто почти полным исключением ^{222}Rn из системы. Точность метода составляет $\pm 2\%$ и $\pm 3\%$ для определения ^{228}Ra и ^{224}Ra, соответственно, а абсолютная чувствительность равна 2 и 0,5 нкю. Методом пользовались для определения распределения этих изотопов в разных продуктах индийской фабрики редкоземельных элементов в Алвей.

ПРИМЕНЕНИЕ МЕТОДА РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНЦИИ В СЛЕДОВОМ АНАЛИЗЕ—II. НАКОПЛЕНИЕ СЛЕДОВ МЕТАЛЛОВ ОСАЖДЕНИЕМ С 1-(2-ПИРИДИЛАЗО)2-НАФТОДОМ:

RICHARD PÜSCHEL, *Talanta*, 1969, **16**, 351.

Резюме—Добавлением спиртового раствора ПАН при pH 10 осаждаются до 100 мкг марганца, железа, кобальта, никеля, меди и цинка. Осадок накопляют на бумажном фильтре, высушивают и определяют элементы прямым измерением рентгеновской флуоресценции. Для каждого элемента приведены чувствительность, точность и повторяемость. Можно определять до 0,1–0,5 мкг каждого элемента в 50 мл раствора.

Metal chelate exchange in the organic phase—III. Extraction and exchange constants of dithizonates and oxinates: Jiří Starý, *Talanta*, 1969, **16**, 359. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehová 7, Czechoslovakia.)

Summary—Reactions between dithizonates and oxinates of Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga and Bi in chloroform have been studied spectrophotometrically. From the exchange constants determined, the extraction constants of metal dithizonates or metal oxinates have been calculated. By this method extraction constants of many metal chelates can be calculated which are difficult to determine by studies of distribution between aqueous and chloroform phases.

An electrical detection system for a spark-source mass spectrograph: R. J. Conzemius and H. J. Svec, *Talanta*, 1969, **16**, 365. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—An electrical detection system has been developed which can be used with the high-frequency spark-source mass spectrograph. Details of the system are discussed and examples are given illustrating its advantages (rapidity and precision). One distinct advantage of electrical detection is that a constant volume of sample material is used for each impurity determination. The system can also be used to assess sample inhomogeneities.

Cation-exchange behaviour of several elements in hydrobromic acid–organic solvent media. J. Korkisch and E. Klakl, *Talanta*, 1969, **16**, 377. (Analytical Institute, University of Vienna IX, Währingstrasse 83, Austria.)

Summary—The cation-exchange characteristics of 19 elements in hydrobromic acid–organic solvent media have been investigated. In these systems the batch distribution coefficients of the metal ions were determined, using the strongly acidic cation-exchange resin Dowex 50, X8. Methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran and acetic acid have been used as the organic solvents. The conditions most suitable for the quantitative separation of the elements are indicated and discussed. Several examples of successful separations are tabulated.

ОБМЕН ХЕЛАТОВ МЕТАЛЛОВ В ОРГАНИЧЕСКОЙ ФАЗЕ—III. КОНСТАНТЫ ЗКСТРАКЦИИ И ОБМЕНА ДИТИЗОНАТОВ И ОКСИНАТОВ:

Jiří Starý, *Talanta*, 1969, **16**, 359.

Резюме—Изучены спектрофотометрическим методом реакции между дитизонатами Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga и Bi в хлороформе. На основе констант обмена рассчитаны константы зкстракции дитизонатов и оксинатов металлов. Зтим методом можно рассчитать константы зкстракции ряда хелатов металлов, которые трудно определять на основе распределения между волой и хлороформом.

ЭЛЕКТРИЧЕСКИЙ ДЕТЕКТОР ДЛЯ МАСС-СПЕКТРОМЕТРА С ИСКРОВЫМ ИСТОЧНИКОМ:

R. J. Conzemius and H. J. Svec, *Talanta*, 1969, **16**, 365.

Резюме—Сконструирована система детектора которой можно пользоваться на высокочастотном масс-спектрометре с искровым источником. Обсуждены детали системы и приведены примеры иллюстрирующие ее преимущества (быстроту и тоуность). Ясным преимуществом электрического детектора является использование постоянного объема пробы для каждого определения примесей. Системой так же можно пользоваться для оценки негомогенности образцев.

КАТИОНООБМЕННЫЕ ХАРАКТЕРИСТИКИ НЕКОТОРЫХ ЭЛЕМЕНТОВ В РАСТВОРАХ БРОМИСТОВОДОРОДНОЙ КИСЛОТЫ И ОРГАНИЧЕСКОГО РАСТВОРИТЕЛЯ:

J. Korkisch and E. Klakl, *Talanta*, 1969, **16**, 377.

Резюме—Были изучены катионообменные характеристики 19 элементов в растворах бромистоводородной кислоты и органического растворителя. В этих системах определены периодические коэффициенти распределения с использованием сильнокислой катионообменной смолы Дауекс 50, X8. Из органических растворителей использованы метиловый, этиловый, н-пропиловый и изопропиловый спирты, метилгликол, ацетон, тетрагидрофуран и уксусная кислота. Указаны и обсуждены наиоолее пригодны условия для количественного разделения элементов. Приведены примеры успешных разделений.

Phenyl 2-(6-methylpyridyl) ketone oxime—A reagent for copper in alkalis: John R. Pemberton and Harvey Diehl, *Talanta*, 1969, **16**, 393. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Phenyl 2-(6-methylpyridyl) ketone oxime (R) can be used for the determination of copper in alkalis, the orange CuR_2 being extracted into isoamyl alcohol and its absorbance measured. Owing to the stereochemical blocking action of the 6-methyl group, iron does not interfere. In acid solution an orange-yellow compound CuR_3 is formed, also extractable into isoamyl alcohol.

1,5-Bis(dicarboxymethylaminomethyl)-2,6-dihydroxynaphthalene as a selective spectrofluorimetric reagent for calcium: B. Buděšínský and T. S. West, *Talanta*, 1969, **16**, 399. (Department of Chemistry, Imperial College, London, S.W.7.)

Summary—1,5-Bis(dicarboxymethylaminomethyl)-2,6-dihydroxynaphthalene (BDDN) forms fluorescent complexes with aluminium, barium, beryllium, calcium, magnesium and strontium. All the complexes have 2:1 metal:ligand ratios. Barium, calcium, magnesium and strontium exhibit maximal fluorescence at pH 11·7, with excitation and emission maxima at 385 and 445 nm respectively. Aluminium and beryllium show maximal fluorescence at pH 5·8 and 5·2 respectively, the excitation and emission maxima being at 370 and 405 nm. The formation of the calcium complex provides a highly sensitive and selective determination of calcium in the range 10–500 ng. The fluorescence measurement of calcium should be made within 5 min of mixing the solutions because of the instability of the reagent at the given pH. Potassium cyanide may be used as a masking agent and ter- or quadrivalent cations should be removed by preliminary extraction with 8-hydroxyquinoline in chloroform at pH 6·0. In such conditions, of 33 cations studied, only magnesium (>20 ng), strontium (>70 ng) and barium (>150 ng) caused interference in the determination of 300 ng of calcium. Among 16 anions examined, only EDTA interfered seriously.

Phosphorescence characteristics of several antimetabolites: L. B. Sanders, J. J. Cetorelli and J. D. Winefordner, *Talanta*, 1969, **16**, 407. (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.)

Summary—Phosphorescence excitation and emission wavelength peaks, lifetimes, limits of detection, and concentration ranges of analytical usefulness of 37 antimetabolites in rigid (77°K) ethanolic solution were determined. Seventeen of the metabolites produced analytically useful phosphorescence, whereas the remaining 20 were of limited or no analytical use.

ФЕНИЛ-2-(6-МЕТИЛПИРИДИЛ)КЕТОНОКСИМ—РЕАКТИВ ДЛЯ МЕДИ В ЩЕЛОЧЯХ:

John R. Pemberton and Harvey Diehl, *Talanta*, 1969, **16**, 393.

Резюме—Фенил-2-(6-метилпиридил) кетоноксимом (**R**) можно пользоваться для определения меди в щелочях, извлечением оранжевого Cu**R**$_2$ изоамиловым спиртом и измерением его светопоглощения. Железо не влияет на определение вследствие защищающего действия 6-метилгруппы. В кислом растворе образуется оранжево-желтое соединение Cu**R**$_3$, которое так же извлекается изоамиовым спиртом.

1,5-БИС(ДИКАРБОКСИМЕТИЛАМИНОМЕТИЛ)-2,6-ДИОКСИНАФТАЛИН КАК СЕЛЕКТИВНЫЙ СПЕКТРОФЛУОРОМЕТРИЧЕСКИЙ РЕАГЕНТ ДЛЯ КАЛЬЦИЯ:

B. Buděšìnský and T. S. West, *Talanta*, 1969, **16**, 399.

Резюме—1,5-Бис(дикарбоксиметиламинометил)-2,6-диоксинафталин образует флуоресцирующие комплексы с алюминием, барием, бериллием, кальцием, магнием и стронцием. Отношение металла и лиганда во всех комплексах 2:1. Барий, кальций, магний и стронций показывают максимум флуоресценции при pH 11,7, имеющий максимумы возбуждения и эмиссии при 385 и 445 нм соответственно. Алюминий и бериллий показывают максимумы флуоресценции при pH 5,8 и 5,2 соответственно имеющие максимумы возбуждения и эмиссии при 370 и 405 нм. Комплекс кальция позволяет высокочувствительное и селективное определение кальция в пределах 10–500 нг. Измерение флуоресценции кальция нужно провести не позднее чем 5 мин. После смешивания растворов вследствие нестабильности реагента при данном pH. Цианидом калия можно пользоваться в качестве маскирующего агента, а трех- и четырехвалентные катионы нужно удалить предварительным извлечением раствором 8-оксихинолина в хлороформе при pH 6,0. В этих условиях из 33 изученных катионов только магий (>20 нг), стронций (>70 нг) и барий (>150 нг) мешают определению 300 нг кальция. Из 16 испытанных анионов только ЭДТА серьёзно мешает определению.

ХАРАКТЕРИСТИКИ ФОСФОРЕСЦЕНЦИИ НЕКОТОРЫХ АНТИМЕТАБОЛИТОВ:

L. B. Sanders, J. J. Cetorelli and J. D. Winefordner, *Talanta*, **16**, 1969, 407.

Резюме—Определены пики возбуждения и эмиссии фосфоресценции, продолжительность, предел определения и пределы концентраций применимых в анализе 37 антиметаболитов в жёстком (77°K) растворе этилового спирта. Семнадцать из этих метаболитов дали применимую в анализе фосфоресценцию, остальные не применими или только ограниченно применими в анализе.

Separation of zirconium by thin-layer chromatography: Koichi Oguma, *Talanta*, 1969, **16**, 409. (Government Chemical Industrial Research Institute, Honmachi, Shibuya-ku, Tokyo, Japan.)

Summary—The thin-layer chromatographic separation of a number of metal ions [Sc, Y, Zr, La, Sm, Th, U(VI), *etc.*] with solvent mixtures of mesityl oxide, ethanol and 5*M* nitric acid on silica gel–cellulose (5:1) thin-layer plates is reported. Zirconium remains stationary whilst the other metal ions move with the solvent, thus allowing a selective separation of zirconium from about 20 metal ions in ratios ranging from 100:1 to 1:100. Mixtures of various metal ions can also be separated.

A highly sensitive extraction–photometric method for nickel with dithizone and phenanthroline: Kumar S. Math, Kashinath S. Bhatki and Henry Freiser, *Talanta*, 1969, **16**, 412. (Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.)

Summary—Addition of phenanthroline to nickel dithizonate in chloroform results in a mixed ligand complex, $NiDz_2phen$, the high molar absorptivity of which (49.1×10^3) results in a colorimetric estimation of nickel that is significantly more sensitive than any other method.

Spectrophotometric determination of copper in plutonium metal with 2,9-dimethyl-1,10-phenanthroline: J. W. Lindsay and C. E. Plock. *Talanta*, 1969, **16**, 414. (The Dow Chemical Company, Rocky Flats Division, Golden, Colorado, U.S.A.)

Summary—A spectrophotometric method for the determination of copper in plutonium has been developed. The copper is complexed with neocuproine, extracted into chloroform, and the absorbance read at 457 mμ. The average relative error of the method is −1·4% with an average relative standard deviation of 4%.

Spectrophotometric determination of selenium with cyclohexanone: M. S. Cresser and T. S. West, *Talanta*, 1969, **16**, 416. (Chemistry Department, Imperial College, London, S.W.7, U.K.)

Summary—Selenium (2–100 μg) can be determined directly in the aqueous phase by formation of the ketone–chloro complex with cyclohexanone in ~7*M* hydrochloric acid from either selenium(IV) or selenium(VI), the reaction being brought to completion by heating for 5 min in a boiling water-bath.

ВЫДЕЛЕНИЕ ЦИРКОНИЯ МЕТОДОМ ТОНКОСЛОЙНОЙ ХРОМАТОГРАФИИ:

KOICHI OGUMA, *Talanta*, 1969, **16**, 409.

Резюме—Описано разделение методом тонкослойной хроматографии ряда ионов металлов (Sc, Y, Zr, La, Sm, Th, U(VI), итп) с смесями окиси мезитила, этилового спирта и 5*M* азотной кислоты на слоях силикагеля и целлюлозы (5:1). Цирконий остается на стартовой линии, в то время как други ионы металлов продвигаются с растворителем. Этим образом получается селективное отделение циркония от 20 ионов металлов в отношениях от 100:1 до 1:100. Возможно также разделение смесей различных ионов металлов.

ВЫСОКОЧУВСТВИТЕЛЬНЫЙ ЭКСТРАКЦИОННО-ФОТОМЕТРИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ НИКЕЛЯ С ИСПОЛЬЗОВАНИЕМ ДИТИЗОНА И ФЕНАНТРОЛИНА:

KUMAR S. MATH, KAHSINATH S. BHATKI and HENRY FREISER, *Talanta*, 1969, **16**, 412.

Резюме—Добавлением фенантролина к дитизонате никеля в хлороформе образуется комплекс с смешанными лигандами $NIDz_2phen$; высоким молярным поглощением комплекса ($49{,}1 \times 10^3$) пользовались для колориметрического определения никеля которое является в значительной мере более чувствительным от какого-либо другого метода.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕДИ В МЕТАЛЛИЧЕСКОМ ПЛУТОНИИ 2,9-ДИМЕТИЛ-1,10-ФЕНАНТРОЛИНОМ:

J. W. LINDSAY and C. E. PLOCK, *Talanta*, 1969, **16**, 414.

Резюме—Разработан спекрофотометрический метод определения меди в плутонии. Медь комплексируют неокупроином, извлекают хлороформом и измеряют светопоглощение при 457 нм. Средная относительная ошибка метода—1,4%, а среднее относительное стандартное откло- нение 4%.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЕЛЕНА ЦИКЛОГЕКСАНОНОМ:

M. S. CRESSER and T. S. WEST, *Talanta*, 1969, **16**, 416.

Резюме—Селен можно определять директно в водной фазе образованием кетон-хлоркомплекса с циклогексаноном в ~7M соляной кислоте из селена(IV) или селена(IV); реакция доводится до конца нагреванием в кипящей водной бане в течение 5 мин.

Mass spectrometry of volatile mercury salts: J. R. Majer, *Talanta*, 1969, **16**, 420. (Chemistry Department, P.O. Box 363, University of Birmingham, Birmingham 15, U.K.)

Summary—The integrated ion current method is applied to the determination of μg quantities of mercury(II) chloride. The mass spectra of both mercury(I) and (II) chlorides indicate that the analytical reagent grade chemicals contain traces of mercury(II) bromide and iodide.

Improved selectivity of chemical colour reactions by simple gas chromatographic separation: J. E. Davies and D. E. Hillman, *Talanta*, 1969, **16**, 421. (Chemical Inspectorate, Ministry of Defence, Royal Arsenal East, Woolwich, S.E.18, U.K.)

Summary—Gas chromatography is applied to improve the selectivity of sensitive organic colour tests without the use of complicated apparatus.

Arsenazo III and its analogues—VI. Some new photometric reagents for palladium: S. B. Savvin, R. F. Propistsova and L. A. Okhanova, *Talanta*, 1969, **16**, 423. (Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, Moscow, U.S.S.R.)

Summary—Colour reactions of palladium with 2,7-bisazo derivatives of chromotropic acid, containing the *o,o'*-dihydroxyazo group, are characterized by high sensitivity (ε = 60–82 $\times 10^3$) and good contrast ($\Delta\lambda$ = 70–80 nm) and permit determination of palladium over a wide range of acidity (from pH 5 to 4N sulphuric acid). Many other metals, including the other platinum metals, do not interfere when present in up to 100-fold amounts.

Determination of caesium-137 in fast-reactor coolant systems: G. Oldham, A. R. Ware and D. J. Sykes, *Talanta*, 1969, **16**, 430. (Department of Chemistry, University of Technology, Loughborough, Leicestershire.)

Summary—A method for the separation of caesium by ion-exchange involving ammonium 12-molybdophosphate has been investigated, and found to be 100% efficient for aqueous solutions with high sodium and potassium concentrations.

Potassium thiocarbonate as a complexing agent and precipitant: K. N. Johri, N. K. Kaushik and Kirpal Singh, *Talanta*, 1969, **16**, 432. (Department of Chemistry, University of Delhi, Delhi-7, India.)

Summary—Efficient analytical separations of Mo(VI), Tl(I), Se(IV), Te(IV) and V(V) from various ions have been made possible by using potassium thiocarbonate (PTC) as a complexing and precipitating agent. For gravimetric estimations, thermogravimetric studies of the products have been used to determine the optimum temperature range of ignition.

МАСС-СПЕКТРОМЕТРИЯ ЛЕТУЩИХ СОЛЕЙ РТУТИ:

J. R. Majer, *Talanta*, 1969, **16**, 420.

Резюме—Автор пользуется методом интегрированного ионного тока для определения микрограммовых количеств хлорида ртути(II). Масс-спектры хлоридов ртути(I) и ртути(II) указивают на присутствие следов бромида и иодида ртути(II) в чистых для анализа реагентах.

УЛУЧШЕНИЕ СЕЛЕКТИВНОСТИ ХИМИЧЕСКИХ ЦВЕТНЫХ РЕАКЦИЙ НЕСЛОЖНЫМ РАЗДЕЛЕНИЕМ С ИСПОЛЬЗОВАНИЕМ ГАЗОВОЙ ХРОМАТОГРАФИИ:

J. E. Davies and D. E. Hillman, *Talanta*, 1969, **16**, 421.

Резюме—Авторы пользовались методом газовой хроматографии для улучшения селективности чувствительных органических цветных реакций без применения сложных приборов.

АРСЕНАЗО III И ЕГО АНАЛОГИ—VI. НЕКОТОРЫЕ НОВЫЕ РЕАГЕНТЫ ДЛЯ ПАЛЛАДИЯ:

S. B. Savvin, R. F. Propistsova and L. A. Okhanova, *Talanta*, 1969, **16**, 423.

Резюме—Цветные реакции палладия с 2,7-бисазопроизводными хромотроповой кислоты, содержающими *o*,*o*’-диоксиазогруппу характеризуются высокой чувствительностью ($\varepsilon = 60–82 \times 10)^3$ и хорошей контрастностью ($\Delta\lambda = 70–80$ нм), и позволяют определять палладий в широком диапазоне кислотности (от pH 5 до 4*N* серной кислоты). Многиес другие металлы, включая платиновые не влияют в 100 кратных и болыих количествах.

ОПРЕДЕЛЕНИЕ ЦЕЗИЯ-137 В ОХЛАЖДАЮЩИХ СИСТЕМАХ БЫСТРЫХ РЕАКТОРОВ:

G. Oldham, A. R. Ware and D. J. Sykes, *Talanta*, 1969, **16**, 430.

Резюме—Исследован метод выделения цезия с использованием ионного обмена на основе 12-молибдофосфата аммония. Метод оказался 100% эффективным для водных растворов содержающих высокие концентрации натрия и калия.

ТИОКАРБОНАТ КАЛИЯ В КАЧЕСТВЕ КОМПЛЕКСООБРАЗУЮЩЕГО И ОСАЖДАЮЩЕГО АГЕНТА:

K. N. Johri, N. K. Kaushik and Kirpal Singh, *Talanta*, 1969, **16**, 432.

Резюме—Эффективное аналитическое отделение Mo(VI), Tl(I), Se(I), Te(I) и V(V) от различных ионов можно провести с использованием тиокарбоната калия (ТКК) в качестве комплексообразующего и осаждающего агента. Для весового анализа пользовались термогравиметрическим изучением продуктов для определения оптимальных пределах температуры обзоливания.

A simple sensitive recording differential refractometer for column chromatography: J. R. Majer, S. Travers and M. Watson, *Talanta*, 1969, **16**, 434. (Chemistry Department, P.O. Box 363, University of Birmingham, Edgbaston, Birmingham 15, U.K.)

Summary—Light passes through a hollow prism containing the sample liquid and is then focussed on a position-sensitive photodiode. Movement of the image due to a change in the refractive index of the sample produces an electrical signal which is recorded directly on a potentiometer recorder.

Determination of aluminium in a "nimonic" alloy by activation with fast neutrons: D. A. Quigley and J. W. A. Trussler, *Talanta*, 1969, **16**, 438. (Chemical Inspectorate, Royal Arsenal East, Woolwich, London, S.E.18.)

Summary—Aluminium at the 6% level was determined in a 15-component "nimonic" alloy with a coefficient of variation of ±8·7% by using fast-neutron activation followed by pulse-height analysis of gamma-ray spectra. The possibility of determining chromium, iron, cobalt and manganese is discussed.

Photometrische Bestimmung von Gold mit Anthranilsäure: Mihail E. Macovschi, *Talanta*, 1969, **16**, 443. (Institut für Physikalische Chemie der Rumänischen Akademie der Wissenschaften, Bukarest 13, str. Galati 31, Rumänien.)

Summary—A colorimetric method is described for the determination of gold as a colloidal solution, with anthranilic acid as reducing agent. The method is rapid and simple, and has the advantage of working in the presence of *aqua regia* used to dissolve the gold. Quantities of 50–1000 μg of gold may be determined.

Radiometric acid–base titrations: L. Erdey, O. Gimesi and F. Szabadváry, *Talanta*, 1969, **16**, 445. (Institute of General and Analytical Chemistry, Technical University, Budapest XI, Gellért tér, 4.)

Summary—Acid–base titrations can be performed with radiometric end-point detection by use of labelled metal salts (*e.g.*, $ZnCl_2$, $HgCl_2$) Owing to the formation or dissolution of the corresponding hydroxide after the equivalence point, the activity of the titrated solution linearly increases or decreases as excess of standard solution is added. The end-point of the titration is determined graphically.

ПРОСТОЙ ЧУВСТВИТЕЛЬНЫЙ САМОПИШУЩИЙ ДИФФЕРЕНЦИАЛЬНЫЙ РЕФРАКТОМЕТР ДЛЯ ХРОМАТОГРАФИИ НА КОЛОНКЕ:

J. R. Majer, S. Travers and M. Watson, *Talanta* 1969, **16**, 434.

Резюме—Луч проходит через полую призму содержащую жидкую пробу а затем фокусируется на чувствительный на местоположение фотодиод. Вызванное переменами показателя преломления передвижение отражения производит электрический сигнал который записывается прямо на потенциометрическом самопишущем приборе.

ОПРЕДЕЛЕНИЕ АЛЮМИНИЯ В "nimonic" СПЛАВЕ РАДИОАКТИВАЦИОННЫМ АНАЛИЗОМ С ИСПОЛЬЗОВАНИЕМ БЫСТРЫХ НЕЙТРОНОВ:

D. A. Quigley and J. W. A. Trussler, *Talanta*, 1969, **16**, 438.

Резюме—Алюминий при концентрации 6% в 15-компонентном "nimonic" сплаве определен с коэффициентом варации ±8,7% активацией с быстрыми нейтронами с последовательным анализом импульсов спектров гамма-лучей. Обсуждена возможность определения хрома, железа, кобальта и марганца.

ФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЗОЛОТА АНТРАНИЛОВОЙ КИСЛОТОЙ:

Mihail E. Macovschi, *Talanta*, 1969, **16**, 443.

Резюме—Описан колориметрический метод определения золота в форме коллоидального раствора, с использованием антраниловой кислоты в качестве восстановителя. Метод является быстрым и несложным, его преимущество в том, что позволяет провести определение в присутствии царской водки, которой пользуются для растворения золота. Этим методом можно определять 50–1000 мкг золота.

РАДИОМЕТРИЧЕСКИЕ КИСЛОТНО-ЩЕЛОЧНЫЕ ТИТРАЦИИ:

L. Erdey, O. Gimesi and F. Szabadváry, *Talanta*, 1969, **16**, 445.

Резюме—Кислотно-щелочные титрации можно проводить с радиометрическим обнаружением конца титрования, с использованием меченых солей металлов (на пример $ZnCl_2$, $HgCl_2$). В зависимости от образования или растворения соответствующей гидроокиси после точки эквиваленции, активность титруемого раствора линейно повышается или снижается с добавлением избытка титрованного раствора. Конец титрования определяется графическим методом.

New chromogens of the ferroin-type—IV. Oximes of substituted methyl and phenyl 2-pyridyl ketones: ALFRED A. SCHILT and PAUL J. TAYLOR, *Talanta*, 1969, **16**, 448. (Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.)

Summary—The spectral characteristics, and solution conditions requisite for formation, of the iron(II), cobalt(II), and copper(I) chelates of some newly synthesized oximes containing the ferroin functional grouping have been determined. For some of the oximes, both *syn*- and *anti*-isomers were available for study. NMR spectra of the isomers differed, enabling structural distinctions to be made. None of the *anti*-isomers formed coloured metal chelates. A practical method for distinguishing between the isomers can be based on these findings. Two of the compounds proved very promising as highly sensitive chromogens for determining iron in strongly alkaline materials.

EDTA titration of tellurium, based on the formation of copper(I) telluride: WEIMAR W. WHITE and JOHN G. SABO, *Talanta*, 1969, **16**, 452. (RCA Electronic Components, Somerville, N.J. 08876, U.S.A.)

Summary—An indirect EDTA titrimetric method is described for the determination of tellurium in thermoelectric materials and synthetic mixtures. Stoichiometric copper(I) telluride is precipitated from a hot acidic solution in the presence of excess of copper(II) chloride and sodium hypophosphite. The method is accurate (mean relative error 0.5%) and selective.

Extractive photometric determination of vanadium with catechol and a tertiary amine: VĚNCESLAV PATROVSKÝ, *Talanta*, 1969, **16**, 456. (Central Geological Survey, Prague, Czechoslovakia.)

Summary—Metal catechol complexes can be extracted from aqueous solution with chloroform in the presence of tertiary amines, for example diphenylguanidine, tributylamine or collidine. Collidine can also be used for the determination of vanadium, titanium, molybdenum and niobium in the presence of a small amount of iron or tantalum. The method for determination of microgram amounts of vanadium is described.

НОВЫЕ ХРОМОГЕНЫ ТИПА ФЕРРОИНА—IV. ОКСИМИ ЗАМЕЩЕННЫХ МЕТИЛ- И ФЕНИЛ-2-ПИРИДИЛКЕТОНОВ:

ALFRED A. SCHILT and PAUL J. TAYLOR, TALANTA 1969, **16**, 448.

Резюме—Определены спектральные характеристики и условия растворов для образования хелатов железа(II), кобальта(II) и меди(I) с некоторыми новосинтезированными оксимами содержащими функциональную группу ферроина. В случае некоторых из оксимов исследовались *СИН*-и*АНТИ*-изомеры. Спектры ЯМР изомеров различались и дали возможность различать структуры. *АНТИ*-изомеры не образовали окрашенные хелаты металлов. Возможно основывать практический метод распознавания изомеров на этих данных. Два из изученных соединений оказались высокочувствительными хромогенами для определения железа в сильно щелочных материалах.

ТИТРАЦИЯ ТЕЛЛУРА С ЭДТА ОСНОВЫВАЮЩАЯСЯ НА ОБРАЗОВАНИИ ТЕЛЛУРИДА МЕДИ(I):

WEIMAR W. WHITE and JOHN G. SABO, *Talanta*, 1969, **16**, 452.

Резюме—Описан косвенный метод титрования с ЭДТА для определения теллура в термоэлектрических веществах и искусственных смесях. Теллурид меди(I) осаждается стехиометрически из горячего кислого раствора в присутствии избытка меди(II) хлорида и натрия гипофосфита. Метод является точным и селективным—средная относительная ошибка равна 0,5%.

ЭКСТРАКЦИОННО-ФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ВАНАДИЯ С ИСПОЛЬЗОВАНИЕМ КАТЕХИНА И ТРЕТИЧНОГО АМИНА:

VĚNCESLAV PATROVSKÝ, *Talanta*, 1969, **16**, 456.

Резюме—Комплексы металлов с катехином извлекаются из водного раствора хлороформом в присутствии третичных аминов, на пример дифенилгуанидина, трибутиламина или коллидина. Коллидином также можно пользоваться для определения ванадия, титана, молибдена и ниобия в присутствии небольших количеств железа или тантала. Описан метод для определения микрограммовых количеств ванадия.

Determination of tungsten by acidimetric titration: ALAN G. SINCLAIR, *Talanta*, 1969, **16**, 459. (Grimsby College of Technology, Nuns' Corner, Grimsby, Lincolnshire, England.)

Summary—A new method is described for the acidimetric titration of tungstate, based on the reaction $x\mathrm{WO_4}^{2-} + x\mathrm{H}^+ +$ mannitol = complex. Quantities of tungsten greater than 2·5 mmole may be determined with a relative standard deviation of not more than 0·1%. The method is subject to interference by any species in the tungstate solution which absorbs protons in the pH range 5·5–8·5.

Spectrophotometric determination of antimony with 3,5,7,4′-tetrahydroxyflavone (kaempferol): B. S. GARG, K. C. TRIKHA and R. P. SINGH, *Talanta*, 1969, **16**, 462. (Department of Chemistry, University of Delhi, Delhi-7, India.)

Summary—A selective spectrophotometric method is described for determination of antimony with kaempferol. Microgram amounts of antimony can be determined by measurements at 420 nm in 0·1M hydrochloric acid. The molar absorptivity is $1{\cdot}09 \times 10^4$ at 420 nm and the optimum range for accurate determination is 1·9–7·8 ppm of antimony.

Microdetermination of carbon and hydrogen—Automatic combustion in a dynamic system: N. E. GEL'MAN, *Talanta*, 1969, **16**, 464. (Institute of Elemental Organic Compounds, Academy of Sciences, Moscow, U.S.S.R.)

Summary—An automatic combustion method has been developed for organic and organo-metallic compounds (5–10 mg samples), based on "wide tube" dynamic combustion in a turbulent oxygen atmosphere. Hydrocarbons, carboranes, transition metal carborane complexes, highly fluorinated compounds, silanes, siloxanes and cyclosilazanes, fluoroderivatives of alkyl phosphinic acids, high polymers, *etc.* have been analysed by it. Silver-plated pumice, magnesium oxide, fibrous asbestos and crushed quartz were used to absorb interfering elements. Advantages over the manual procedure are simplicity of procedure, rapid combustion of difficultly combustible or highly volatile compounds, and better reproducibility of the results. The overall combustion cycle takes 15 min. The standard deviation for hydrogen is 0·01–0·15% and for carbon is 0·10–0·23% (carbon content 20–95%).

ОПРЕДЕЛЕНИЕ ВОЛЬФРАМА АЦИДИМЕТРИЧЕСКИМ ТИТРОВАНИЕМ:

ALAN. G SINCLAIR, *Talanta*, 1969, **16**, 459.

Резюме—Описан новый метод ацидиметрического титрования вольфрамата, основывающийся на реакции $x\mathrm{WO_4}^{2-} + x\mathrm{H}^+ +$ маннитол = комплекс. Можно определять больше чем 2,5 ммоля вольфрама с относительной стандартной ошибкой меньше чем 0,1%. Метод подверженный влиянию каждого вещества в растворе вольфрама, абсорбирующего протоны в области pH 5,5–8,5.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СУРЬМЫ 3,5,7,4′-ТЕТРАОКСИФЛАВОНОМ (КЕМПФЕРОЛОМ):

B. S. GARG, K. C. TRIKHA and R. P. SINGH, *Talanta*, 1969, **16**, 462.

Резюме—Описан избирательный спекрофотометрический метод определения сурьмы кемпферодом. Можно определять микрограммовые количества сўрмы измерением светопоглощения при 420 нм в 0,1*M* соляной кислоте. Молярное поглощение $1{,}09 \times 10^4$ при 420 нм, а оптимальные пределы концентрации для точного определения 1,9–7,8 мг/л сурьмы.

МИКРООПРЕДЕЛЕНИЕ УГЛЕРОДА И ВОДОРОДА—АВТОМАТИЧЕСКОЕ СЖИГАНИЕ В ДИНАМИЧЕСКОЙ СИСТЕМЕ:

N. E. Gel'man, *Talanta*, 1969, **16**, 464.

Резюме—Разработан автоматический метод сжигания органических и металлоорганических соединений (пробы 5–10 мг), основывающийся на динамическом сжигании в турбулентной атмосфере кислорода. Метод применен в анализе углеводородов, карборанов, карборановых комплексов переходных металлов, высокофторированных соединений, силанов, силоксанов и циклосилазанов, фтористых дериватов алкилфосфиновых кислот, высокомолекулярных соезинений, и т.д. Мешающие элементы абсорбировались на покрытой серебром пемзе, окиси магния, волокнистом асбесте и дроблёном кварце. Преимущества метода в сравнении с ручным методом—простая процедура, быстрое сжигание трудносжигаемых соединений и улучшенная воспроизводимость результатов. Продолжительность цикла сжигания 15 мин. Стандартная ошибка для водорода 0,01–0,15%, а для углерода 0,10–0,15% (содержание углерода 20–95%).

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