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# Journal of Inorganic and Nuclear Chemistry

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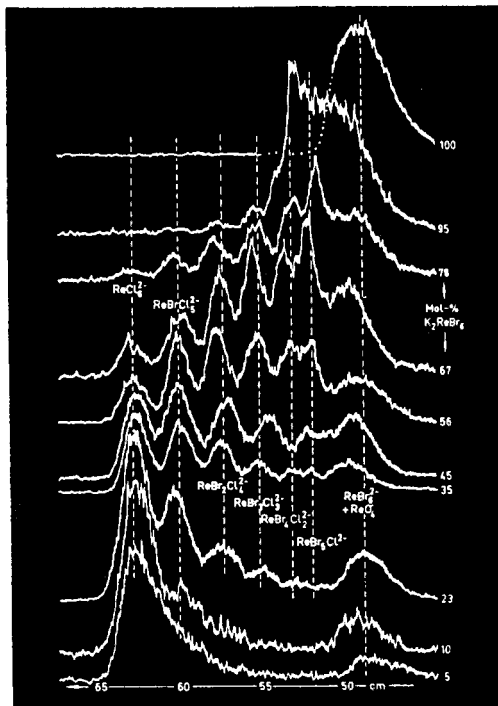
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An International Journal of Analytical Chemistry



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## ZUM KONVERGENZBEREICH DER ITERATIVEN ERMITTLUNG SUKZESSIVER PROTONIERUNGS- KONSTANTEN UND ZU DEREN RELATIVER REIHENFOLGE

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(Eingegangen am 31. August 1970. Angenommen am 28. April 1971)

**Zusammenfassung**—In dieser Arbeit werden unabhängig voneinander Beziehungen aus einem logarithmischen Iterationsverfahren und aus einem numerischen Verfahren zur Berechnung von Säuredissoziations- bzw. Komplexstabilitätskonstanten abgeleitet, aus denen sich die relative Lage der  $pK$ - bzw.  $\log K$ -Werte zueinander aus den pH-Differenzen bei  $\bar{n} = 0,5; 1,5$  und  $2,5$  abschätzen läßt. Der Konvergenzbereich des logarithmischen Iterationsverfahrens wird in Abhängigkeit von den oben genannten pH-Differenzen hergeleitet. Für die Grenzwerte der Iteration werden geschlossene Ausdrücke für beliebige Wertepaare ( $pH, \bar{n}$ ) angegeben.

ZUR DIGITALEN-AUSWERTUNG von potentiometrischen Komplexbildungs- und Säuredissoziationsdaten existieren Computerprogramme.<sup>1,2</sup> Neben der maschinellen Berechnung der Säuredissoziations- und Komplexstabilitätskonstanten ist aber immer noch die "manuelle" Berechnung üblich bzw. letztere wird vor der exakten Berechnung zur Abschätzung der zu erwartenden Werte der Konstanten verwendet. Dabei treten Komplikationen auf, wenn sich zwei aufeinanderfolgende Konstanten (wegen der Analogie von Protonierung eines Liganden und Komplexbildung kann man Stabilitätskonstanten und Säuredissoziationskonstanten zusammen betrachten) um weniger als den Faktor 1000 unterscheiden und die Konstanten nicht isoliert, d.h. unabhängig voneinander berechnet werden können. Je nach verwendetem Rechenverfahren muß man größere Gleichungssysteme lösen oder mehrere Iterationen ausführen. Je geringer der Unterschied zweier aufeinanderfolgender Konstanten ist, desto mehr verschmelzen die beiden zugehörigen Puffergebiete, und in der potentiometrischen Titrationskurve ist nur noch ein Puffergebiet erkennbar. Es gibt bereits mehrere Arbeiten, die aus der Titrationskurve bestimmte pH-Werte herausgreifen und als Kriterien für die Abschätzung der zu erwartenden Werte der Konstanten heranziehen.<sup>3-6</sup> Als markante Punkte der Titrationskurve wurden jeweils die pH-Werte bei  $\bar{n} = n - 0,5$  verwendet. Die z.T. empirisch, z.T. rechnerisch ermittelten Werte sind nicht widerspruchsfrei.

In dieser Arbeit werden Beziehungen abgeleitet, die gestatten, aus den pH-Werten bei  $\bar{n} = n - 0,5$  zu errechnen, wann die Konstanten in der üblichen Reihenfolge ( $pK_n > pK_{n-1}$ ), in vertauschter Reihenfolge ( $pK_n < pK_{n-1}$ ) und wann physikalisch-chemisch sinnlose (negative) Konstanten resultieren. Davon nicht zu trennen ist die Untersuchung des Iterationsverfahrens zur  $pK$ -Wert-Berechnung auf Konvergenzbereich und damit auf Anwendbarkeit.

Die Grundlage der Berechnungen von sukzessiven Protonierungskonstanten ist das Bjerrum'sche Verfahren,<sup>7</sup> dessen Bestimmungsgleichungen entweder numerisch oder nach einem logarithmischen Iterationsverfahren ausgewertet werden können.<sup>8</sup>

Wie in den bereits zitierten Arbeiten verwenden wir als besondere Kriterien einer

Titrationkurve die pH-Werte bei  $\bar{n} = n - 0,5$  und als besondere Kriterien einer Bildungskurve die pA-Werte bei  $\bar{n} = n - 0,5$  (im folgenden werden die  $\bar{n}$ -Werte als Indices an pH und pA verwendet). Aus der allgemeinen Beziehung

$$pK_n = \text{pH} + \log \frac{\bar{n} - n + 1}{n - \bar{n}}$$

ergeben sich durch zweimalige Differentiation nach  $\bar{n}$  die Minima der Fehler für  $\bar{n} = n - 0,5$ .

#### Berechnungen zum logarithmischen Iterationsverfahren

Bhatt und Mitarbeiter<sup>5</sup> untersuchten das logarithmische Iterationsverfahren auf Konvergenz. Sie fanden für eine vorgegebene Differenz  $\text{pH}_{0,5} - \text{pH}_{1,5} = 0,8$  noch Konvergenz, für eine Differenz von 0,7 Konvergenz, aber  $\text{p}K_1 > \text{p}K_2$ . Sie schlußfolgerten daraus, daß man bei einer Differenz  $< 0,8$  nicht mehr zwischen  $\text{p}K_1$  und  $\text{p}K_2$  unterscheiden und dieses und auch jedes andere Verfahren nicht mehr anwenden könne. Ein Grenzwert für die Konvergenz war aber nicht gegeben.

Schröder<sup>6</sup> untersuchte das Iterationsverfahren ebenfalls auf Konvergenz und führte die Iterationen für vorgegebene Differenzen  $\text{p}A_{0,5} - \text{p}A_{1,5}$  maschinell durch. Für eine Differenz von 0,477 ( $[A]_{1,5} = 3[A]_{0,5}$ ) tritt bei einer Genauigkeit von 0,001 nach 988 Iterationen Konvergenz ein. Für  $\text{p}A_{0,5} - \text{p}A_{1,5} < 0,477$  beobachtet er Divergenz, für  $\text{p}A_{0,5} - \text{p}A_{1,5} = 0,724$  werden  $\log k_1$  und  $\log k_2$  gleich. Außerdem gibt Schröder für  $k_1$  und  $k_2$  zwei geschlossene Ausdrücke des Grenzwertes der Iteration an, die man numerisch durch Lösen eines linearen Gleichungssystems mit  $\bar{n} = 0,5$  und  $\bar{n} = 1,5$  errechnen kann.

Im folgenden werden Berechnungen an zwei- und dreibasigen Säuren sowohl nach dem logarithmischen Iterationsverfahren als auch nach dem numerischen Verfahren und Berechnungen an Komplexbildungsgleichgewichten nach dem logarithmischen Iterationsverfahren ausgeführt und kritisch mit den aus der Literatur bekannten Ergebnissen verglichen.

Zur Berechnung an zweibasigen Säuren gehen wir von folgenden Gleichungen aus:

$$\text{p}K_1 = \text{pH}_{\bar{n}_1} + \log \frac{\bar{n}_1 - 1}{2 - \bar{n}_1} + \log \left[ 1 + \frac{K_2}{[\text{H}^+]_{\bar{n}_1}} \cdot \frac{\bar{n}_1}{\bar{n}_1 - 1} \right] \quad (1)$$

$$\text{p}K_2 = \text{pH}_{\bar{n}_2} + \log \frac{\bar{n}_2}{1 - \bar{n}_2} - \log \left[ 1 + \frac{[\text{H}^+]_{\bar{n}_2}}{K_1} \cdot \frac{2 - \bar{n}_2}{1 - \bar{n}_2} \right] \quad (2)$$

Mit  $\bar{n}_1 = 1,5$  bzw.  $\bar{n}_2 = 0,5$  nehmen Gl. (1), (2) folgende Form an:

$$\text{p}K_1 = \text{pH}_{1,5} + \log \left[ 1 + \frac{3K_2}{[\text{H}^+]_{1,5}} \right] \quad (3)$$

$$\text{p}K_2 = \text{pH}_{0,5} - \log \left[ 1 + \frac{3[\text{H}^+]_{0,5}}{K_1} \right] \quad (4)$$

Für jeden speziellen Fall sind die pH-Werte bei  $\bar{n} = 1,5$  bzw. 0,5 Konstanten, so daß die Konvergenzbetrachtung an den Korrekturgliedern ( $\log [1 + \dots]$ ) durchgeführt werden muß. Die Zahlenfolge der Korrekturglieder konvergiert dann, wenn die Numeri konvergieren.

Wir setzen  $[\text{H}^+]_{0,5} = x$  und  $[\text{H}^+]_{1,5} = y$  und erhalten damit aus den Gl. (3), (4) durch Entlogarithmierung

$$K_2 = x + \frac{3x^2}{K_1} \quad (5)$$

$$\frac{1}{K_1} = \frac{1}{y} + \frac{3K_2}{y^2} \quad (6)$$

Setzen wir Gl. (5), (6) abwechselnd in die Korrekturglieder von Gl. (3), (4) ein, erhalten wir für beide dieselbe geometrische Reihe der Numeri:

$$1 + 3 \frac{x}{y} + 9 \frac{x^2}{y^2} + 27 \frac{x^3}{y^3} + 81 \frac{x^4}{y^4} + \dots \quad (7)$$

$$\text{mit } a_n = \left[ \frac{3x}{y} \right]^{n-1}, \quad q = \frac{3x}{y}$$

Eine geometrische Reihe konvergiert für  $q < 1$ , so daß Gl. (7) für  $y > 3x$  ( $[\text{H}^+]_{1,5} > 3[\text{H}^+]_{0,5}$ ) konvergiert.

Die Summe der geometrischen Reihe (7) beträgt  $S = y/(y - 3x)$ . Damit können für  $pK_1$  und  $pK_2$  geschlossene Ausdrücke angegeben werden, die eine Iteration erübrigen, da sie bereits den Grenzwert angeben.

Nach Resubstitution von  $y$  und  $x$  erhält man

$$pK_1 = \text{pH}_{1,5} + \log \left[ \frac{[\text{H}^+]_{1,5}}{[\text{H}^+]_{1,5} - 3[\text{H}^+]_{0,5}} \right] \quad (8)$$

$$pK_2 = \text{pH}_{0,5} - \log \left[ \frac{[\text{H}^+]_{1,5}}{[\text{H}^+]_{1,5} - 3[\text{H}^+]_{0,5}} \right] \quad (9)$$

Man erhält  $pK_1 = pK_2$ , wenn

$$\text{pH}_{0,5} - \text{pH}_{1,5} = 2 \log \left[ \frac{[\text{H}^+]_{1,5}}{[\text{H}^+]_{1,5} - 3[\text{H}^+]_{0,5}} \right]$$

Mit  $a = [\text{H}^+]_{1,5}/[\text{H}^+]_{0,5}$  erhalten wir daraus die Gleichung

$$a^2 - 7a + 9 = 0 \quad (10)$$

mit den Wurzeln  $a_1 = 5,3 \dots$ ,  $a_2 = 1,7 \dots$ ;  $a_2$  liegt außerhalb des Konvergenzbereiches und außerhalb reeller Werte der Konstanten, da nach Einsetzen in die Korrekturglieder von Gl. (8), (9) diese negative Werte annehmen, von denen kein Logarithmus gebildet werden kann. Der Wert  $a_1 = 5,3$  bedeutet  $\text{pH}_{0,5} - \text{pH}_{1,5} = 0,724 \dots$ . Erbringt das Experiment eine kleinere pH-Differenz, ist  $pK_2 < pK_1$ .

Gleichungen (8), (9) gelten nur für  $\bar{n}_1 = 1,5$ ;  $\bar{n}_2 = 0,5$ . In der Praxis verwendet man aber Werte von  $0,3 < \bar{n}_2 < 0,7$  und  $1,3 < \bar{n}_1 < 1,7$ . Gleichungen (8), (9) sollen nun verallgemeinert werden. Durch Entlogarithmierung erhält man aus Gl. (1), (2)

$$\frac{1}{K_1} = \frac{\bar{n}_1 - 1}{(2 - \bar{n}_1)[\text{H}^+]_{\bar{n}_1}} \left[ 1 + \frac{K_2 \bar{n}_1}{[\text{H}^+]_{\bar{n}_1}(\bar{n}_1 - 1)} \right] \quad (11)$$

und

$$K_2 = \frac{(1 - \bar{n}_2)[\text{H}^+]_{\bar{n}_2}}{\bar{n}_2} \left[ 1 + \frac{[\text{H}^+]_{\bar{n}_2}(2 - \bar{n}_2)}{K_1(1 - \bar{n}_2)} \right] \quad (12)$$

Setzt man Gl. (11), (12) abwechselnd in das Korrekturglied von Gl. (1) ein, erhält

man mit  $x = [H^+]_{\bar{n}_2}$ ,  $y = [H^+]_{\bar{n}_1}$  folgende Reihe:

$$R = 1 + \frac{\bar{n}_1(1 - \bar{n}_2)x}{\bar{n}_2(\bar{n}_1 - 1)y} + \frac{\bar{n}_1(2 - \bar{n}_2)x^2}{\bar{n}_2(2 - \bar{n}_1)y^2} + \frac{\bar{n}_1^2(1 - \bar{n}_2)(2 - \bar{n}_2)x^3}{\bar{n}_2^2(\bar{n}_1 - 1)(2 - \bar{n}_1)y^3} + \frac{\bar{n}_1^2(2 - \bar{n}_2)^2x^4}{\bar{n}_2^2(2 - \bar{n}_1)^2y^4} + \dots \quad (13)$$

Diese Reihe läßt sich als geometrische Reihe darstellen:

$$R = \left[ 1 + \frac{(1 - \bar{n}_2)\bar{n}_1x}{(\bar{n}_1 - 1)\bar{n}_2y} \right] \sum_{n=0}^{\infty} \left[ \frac{\bar{n}_1(2 - \bar{n}_2)x^2}{\bar{n}_2(2 - \bar{n}_1)y^2} \right]^n \quad (14)$$

Sie konvergiert für  $q < 1$ , d.h.  $[H^+]_{\bar{n}_1} > \sqrt{\frac{\bar{n}_1(2 - \bar{n}_2)}{\bar{n}_2(2 - \bar{n}_1)}} \cdot [H^+]_{\bar{n}_2}$ .

Die Summe von  $R$  beträgt

$$S = \frac{1 + (1 - \bar{n}_2)\bar{n}_1x/(\bar{n}_1 - 1)\bar{n}_2y}{1 - \bar{n}_1(2 - \bar{n}_2)x^2/\bar{n}_2(2 - \bar{n}_1)y^2}$$

Durch Einsetzen von Gl. (11), (12) in das Korrekturglied von Gl. (2) erhält man

$$R' = \left[ 1 + \frac{(2 - \bar{n}_2)(\bar{n}_1 - 1)x}{(2 - \bar{n}_1)(1 - \bar{n}_2)y} \right] \sum_{n=0}^{\infty} \left[ \frac{\bar{n}_1(2 - \bar{n}_2)x^2}{\bar{n}_2(2 - \bar{n}_1)y^2} \right]^n \quad \text{mit} \quad (15)$$

$$S' = \frac{1 + (2 - \bar{n}_2)(\bar{n}_1 - 1)x/(2 - \bar{n}_1)(1 - \bar{n}_2)y}{1 - \bar{n}_1(2 - \bar{n}_2)x^2/\bar{n}_2(2 - \bar{n}_1)y^2}$$

Setzt man  $S$  und  $S'$  in die Korrekturglieder von Gl. (1), (2) ein, erhält man schließlich für  $pK_1$  und  $pK_2$  geschlossene Ausdrücke, die deren Berechnung ohne Iteration ermöglichen.

$$pK_1 = pH_{\bar{n}_1} + \log \frac{\bar{n}_1 - 1}{2 - \bar{n}_1} + \log \left[ \frac{1 + \frac{(1 - \bar{n}_2)\bar{n}_1[H^+]_{\bar{n}_2}}{(\bar{n}_1 - 1)\bar{n}_2[H^+]_{\bar{n}_1}}}{1 - \frac{\bar{n}_1(2 - \bar{n}_2)[H^+]_{\bar{n}_2}^2}{\bar{n}_2(2 - \bar{n}_1)[H^+]_{\bar{n}_1}^2}} \right] \quad (16)$$

$$pK_2 = pH_{\bar{n}_2} + \log \frac{\bar{n}_2}{1 - \bar{n}_2} - \log \left[ \frac{1 + \frac{(2 - \bar{n}_2)(\bar{n}_1 - 1)[H^+]_{\bar{n}_2}}{(2 - \bar{n}_1)(1 - \bar{n}_2)[H^+]_{\bar{n}_1}}}{1 - \frac{\bar{n}_1(2 - \bar{n}_2)[H^+]_{\bar{n}_2}^2}{\bar{n}_2(2 - \bar{n}_1)[H^+]_{\bar{n}_1}^2}} \right] \quad (17)$$

Gleichungen (16), (17) werden mit  $\bar{n}_1 = 1,5$  und  $\bar{n}_2 = 0,5$  mit Gl. (8), (9) identisch.

Zur Berechnung an dreibasigen Säuren verwenden wir folgende Gleichungen:

$$pK_1 = pH_{\bar{n}_1} + \log \frac{\bar{n}_1 - 2}{3 - \bar{n}_1} + \log \left[ 1 + \frac{(\bar{n} - 1)K_2}{(\bar{n} - 2)[H^+]_{\bar{n}_1}} + \frac{\bar{n}_1K_2K_3}{(\bar{n}_1 - 2)[H^+]_{\bar{n}_1}^2} \right] \quad (18)$$

$$pK_2 = pH_{\bar{n}_2} + \log \frac{\bar{n}_2 - 1}{2 - \bar{n}_2} + \log \left[ 1 + \frac{\bar{n}_2K_3}{(\bar{n}_2 - 1)[H^+]_{\bar{n}_2}} \right] - \log \left[ 1 + \frac{(3 - \bar{n}_2)[H^+]_{\bar{n}_2}}{(2 - \bar{n}_2)K_1} \right] \quad (19)$$

$$pK_3 = pH_{\bar{n}_3} + \log \frac{\bar{n}_3}{1 - \bar{n}_3} - \log \left[ 1 + \frac{(2 - \bar{n}_3)[H^+]_{\bar{n}_3}}{(1 - \bar{n}_3)K_2} + \frac{(3 - \bar{n}_3)[H^+]_{\bar{n}_3}^2}{(1 - \bar{n}_3)K_1K_2} \right] \quad (20)$$



Die Konvergenzbetrachtung des Iterationsverfahrens für dreibasige Säuren ist schwieriger als die für zweibasige Säuren, da es sich um ein Problem mit 3 Variablen ( $[H^+]_{2,5}$ ,  $[H^+]_{1,5}$ ,  $[H^+]_{0,5}$ ) handelt. Wir suchen die geringste Differenz  $pH_{0,5} - pH_{2,5}$ , die noch endliche Grenzwerte beim Iterieren liefert.  $pH_{1,5}$  liegt zwischen  $pH_{2,5}$  und  $pH_{0,5}$ , und da in sehr flachen, stark überlappenden Puffergebieten  $pH_{1,5} \approx (pH_{2,5} + pH_{0,5})/2$  gilt, wählen wir für die Rechnung

$$pH_{1,5} = (pH_{2,5} + pH_{0,5})/2 \quad (21)$$

und können dadurch 1 Variable ausschalten.

Wir setzen wieder  $[H^+]_{0,5} = x$ ,  $[H^+]_{1,5} = y$  und  $[H^+]_{2,5} = z$ . Dann wird  $pK_2$  mit Gl. (21) nach Gl. (19) gleich  $pH_{1,5}$ . Die Korrekturglieder für  $pK_1$  und  $pK_3$  werden gleich. Entlogarithmiert ergeben Gl. (18), (20) mit  $\bar{n}_1 = 2,5$  bzw.  $\bar{n}_3 = 0,5$

$$\frac{1}{K_1} = \frac{1}{z} \left[ 1 + \frac{3y}{z} + \frac{5y}{z^2} \cdot K_3 \right] \quad (22)$$

$$K_3 = x \left[ 1 + \frac{3x}{y} + \frac{5x^2}{y} \cdot \frac{1}{K_1} \right]. \quad (23)$$

Setzt man Gl. (22), (23) abwechselnd in das Korrekturglied von Gl. (18) oder Gl. (20) ein, erhält man die Reihe

$$R = 1 + \frac{3y}{z} + \frac{5xy}{z^2} + \frac{15x^2}{z^2} + \frac{25x^3}{z^3} + \frac{75x^3y}{z^4} + \frac{125x^4y}{z^5} + \frac{375x^5}{z^5} \\ + \frac{625x^6}{z^6} + \frac{1875x^6y}{z^7} + \frac{3125x^7y}{z^8} + \dots \text{ bzw.}$$

$$R = \left[ \frac{3z}{5x} + 1 + \frac{3y}{z} + \frac{5xy}{z^2} \right] \sum_{n=0}^{\infty} \left[ \frac{25x^3}{z^3} \right]^n - \frac{3z}{5x} \quad (24)$$

$R$  konvergiert für  $25x^3/z^3 < 1$  bzw.  $z > \sqrt{25x}$ . Dieser Wert entspricht einer Differenz  $pH_{0,5} - pH_{2,5} > 0,466$ . Der Grenzwert des Korrekturgliedes von Gl. (18) lautet unter Verwendung von Gl. (24)

$$\log \left[ \frac{3z/5x + 1 + 3y/z + 5xy/z^2}{1 - 25x^3/z^3} - \frac{3z}{5x} \right]$$

Zur Berechnung der Differenz  $pH_{0,5} - pH_{2,5}$ , aus der  $pK_1 = pK_2 = pK_3$  resultieren, setzen wir

$$[H^+]_{2,5}/K_{1,2,3} = K_{1,2,3}/[H^+]_{0,5} = a$$

in Gl. (22) oder Gl. (23) ein. Es resultiert

$$a^3 - a^2 - 3a - 5 = 0 \quad (25)$$

mit der einzigen reellen Wurzel  $a_1 = 2,751$ . Dieser Wert liefert die gesuchte pH-Differenz  $pH_{0,5} - pH_{2,5} = 0,878$ , da mit  $a > a_1$   $pK_3 > pK_2 > pK_1$ , mit  $a < a_1$   $pK_1 > pK_2 > pK_3$  resultieren.

Zur Untersuchung des logarithmischen Iterationsverfahrens zur Berechnung von Metallchelastabilitätskonstanten auf Konvergenz wurden folgende Gleichungen verwendet:

$$\log k_1 = pA_{\bar{n}_1} + \log \frac{\bar{n}_1}{1 - \bar{n}_1} - \log \left[ 1 + \frac{(2 - \bar{n}_1)k_2[A]_{\bar{n}_1}}{1 - \bar{n}_1} \right] \tag{26}$$

$$\log k_2 = pA_{\bar{n}_2} + \log \frac{\bar{n}_2 - 1}{2 - \bar{n}_2} + \log \left[ 1 + \frac{\bar{n}_2}{(\bar{n}_2 - 1)k_1[A]_{\bar{n}_2}} \right]. \tag{27}$$

Wir verzichten hier auf die ausführliche Berechnung, da sie der oben gegebenen analog ist. Mit  $x = [A]_{\bar{n}_1}$  und  $y = [A]_{\bar{n}_2}$  ( $0,3 < \bar{n}_1 < 0,7$ ,  $1,3 < \bar{n}_2 < 1,7$ ; unterschiedliche Wertebereiche der  $\bar{n}$  zu denen für die Berechnung an zweibasigen Säuren!) erhält man für das Korrekturglied von Gl. (26) die Reihe

$$R_1 = \left[ 1 + \frac{(2 - \bar{n}_1)(\bar{n}_2 - 1)x}{(1 - \bar{n}_1)(2 - \bar{n}_2)y} \right] \sum_{n=0}^{\infty} \left[ \frac{(2 - \bar{n}_1)\bar{n}_2 x^2}{(2 - \bar{n}_2)\bar{n}_1 y^2} \right]^n$$

und für das Korrekturglied von Gl. (27) die Reihe

$$R_2 = \left[ 1 + \frac{\bar{n}_2(1 - \bar{n}_1)x}{\bar{n}_1(\bar{n}_2 - 1)y} \right] \sum_{n=0}^{\infty} \left[ \frac{(2 - \bar{n}_1)\bar{n}_2 x^2}{(2 - \bar{n}_2)\bar{n}_1 y^2} \right]^n$$

Wenn wir die Summen dieser geometrischen Reihen berücksichtigen, können wir Gl. (26), (27) als geschlossene Ausdrücke für  $k_1$  und  $k_2$  formulieren, die keine Iteration mehr erfordern.

$$\log k_1 = pA_{\bar{n}_1} + \log \frac{\bar{n}_1}{1 - \bar{n}_1} - \log \left[ \frac{1 + \frac{(2 - \bar{n}_1)(\bar{n}_2 - 1)[A]_{\bar{n}_1}}{(1 - \bar{n}_1)(2 - \bar{n}_2)[A]_{\bar{n}_2}}}{1 - \frac{(2 - \bar{n}_1)\bar{n}_2[A]_{\bar{n}_1}^2}{(2 - \bar{n}_2)\bar{n}_1[A]_{\bar{n}_2}^2}} \right] \tag{28}$$

$$\log k_2 = pA_{\bar{n}_2} + \log \frac{\bar{n}_2 - 1}{2 - \bar{n}_2} + \log \left[ \frac{1 + \frac{\bar{n}_2(1 - \bar{n}_1)[A]_{\bar{n}_1}}{\bar{n}_1(\bar{n}_2 - 1)[A]_{\bar{n}_2}}}{1 - \frac{(2 - \bar{n}_1)\bar{n}_2[A]_{\bar{n}_1}^2}{(2 - \bar{n}_2)\bar{n}_1[A]_{\bar{n}_2}^2}} \right]. \tag{29}$$

Aus  $q = \bar{n}_2(2 - \bar{n}_1)x^2/\bar{n}_1(2 - \bar{n}_2)y^2$  (aus  $R_1$  und  $R_2$ ) und  $q < 1$  erhalten wir die Konvergenzbedingung

$$[A]_{\bar{n}_2} > \sqrt{\frac{\bar{n}_2(2 - \bar{n}_1)}{\bar{n}_1(2 - \bar{n}_2)}} [A]_{\bar{n}_1}.$$

Setzt man  $\bar{n}_1 = 0,5$  und  $\bar{n}_2 = 1,5$  ein, ergibt sich eine Differenz der  $pA$ -Werte der Bildungskurve von

$$pA_{0,5} - pA_{1,5} > 0,477.$$

Dieser Wert wurde in Analogie zu dem für zweibasige Säuren errechneten Wert erwartet.

Durch Einsetzen von  $\bar{n}_1 = 0,5$  und  $\bar{n}_2 = 1,5$  in Gl. (28), (29) kann man geschlossene Ausdrücke für  $\log k_1$  und  $\log k_2$  in vereinfachter Form aufstellen, die den

Gl. (8), (9) ähnlich sind und den von Schröder<sup>6</sup> in entlogarithmierter Form gegebenen Ausdrücken entsprechen.

Das Berechnungsverfahren für 1:3-Chelate wurde nicht untersucht, da völlig analoge Resultate wie bei der Berechnung an dreibasigen Säuren erwartet werden.

### Berechnungen am numerischen Lösungsverfahren

Wir wollen uns noch einmal der Frage zuwenden: Wie klen müssen die Differenzen  $\text{pH}_{0,5} - \text{pH}_{1,5}$  oder wie flach müssen die Titrationskurven sein, damit  $\text{p}K$ -Werte in vertauschter Reihenfolge oder negative Konstanten errechnet werden? Zuerst wird die Berechnung für eine zweibasige Säure (oder einen Titrationskurventeil einer mehrbasigen Säure, den man wegen seiner isolierten Lage als Titrationskurve einer zweibasigen Säure auffassen kann) ausgeführt, und wir verwenden folgendes Gleichungssystem:

$$\begin{aligned} \bar{n}_2 K_1 K_2 + (\bar{n}_2 - 1)[\text{H}^+]_{\bar{n}_2} K_1 &= (2 - \bar{n}_2)[\text{H}^+]_{\bar{n}_2}^2 \\ \bar{n}_1 K_1 K_2 + (\bar{n}_1 - 1)[\text{H}^+]_{\bar{n}_1} K_1 &= (2 - \bar{n}_1)[\text{H}^+]_{\bar{n}_1}^2 \end{aligned} \quad (30)$$

$$(0,3 < \bar{n}_2 < 0,7; \quad 1,3 < \bar{n}_1 < 1,7).$$

Wir lösen das Gleichungssystem (30) unter Benutzung der Kramer'schen Regel für  $\bar{n}_1 = 1,5$  und  $\bar{n}_2 = 0,5$  und setzen wieder  $x = [\text{H}^+]_{0,5}$  und  $y = [\text{H}^+]_{1,5}$ . Das Verhältnis der Konstanten ergibt sich zu

$$K_1/K_2 = D_{K_1^2}/D \cdot D_{K_1 K_2}.$$

( $D$  ist die Koeffizientendeterminante,  $D_{K_1}$  und  $D_{K_1 K_2}$  sind die zur Berechnung von  $K_1$  und  $K_1 K_2$  notwendigen Det.) bzw.

$$\frac{K_1}{K_2} = \frac{(0,25y^2 - 2,25x^2)^2}{(0,25y + 0,75x)(0,75x^2y + 0,25xy^2)}. \quad (31)$$

Zur Berechnung der  $\text{pH}$ -Differenz, für die  $K_1 = K_2$  wird, setzen wir  $K_1/K_2 = 1$  und erhalten aus Gl. (31)

$$y^4 - y^3x - 24y^2x^2 - 9yx^3 + 81x^4 = 0.$$

Diese Gleichung läßt sich umformen zu

$$(y + 3x)^2(y^2 - 7yx + 9x^2) = 0. \quad (32)$$

Daraus ergeben sich die Lösungen

$$y_{1,2} = -3x, \quad y_3 = 1,7x, \quad y_4 = 5,3x.$$

Die Wurzeln  $y_{1,2}$  können *a priori* als physikalisch-chemisch sinnlos ausgeschlossen werden. Die Wurzeln  $y_3$  und  $y_4$  sind denen von Gl. (10) gleich, da beide Gleichungen (10), (32) mit  $a = y/x$  identisch werden.

Für das Gleichungssystem (30) sind  $D$  und  $D_{K_1 K_2}$  immer positiv.  $D_{K_1}$  kann theoretisch negative Werte annehmen.

Für  $D_{K_1} > 0 \rightarrow K_1 > 0, \rightarrow K_2 > 0$

$D_{K_1} < 0 \rightarrow K_1 < 0, \rightarrow K_2 < 0.$

Setzt man in  $D_{K_1} = 0,25y^2 - 2,25x^2$   $D_{K_1} = 0$ , erhält man mit  $y = 3x$  die Diskriminante für den Vorzeichenwechsel von  $K_1$  (und damit auch von  $K_2$ ).

Aus diesem Verhältnis und den Lösungen von Gl. (32) ergeben sich nach Re-substitution folgende Fälle:

$$\begin{aligned} [\text{H}^+]_{1,5} &> 5,3[\text{H}^+]_{0,5} && \rightarrow pK_1 < pK_2 \\ [\text{H}^+]_{1,5} &= 5,3[\text{H}^+]_{0,5} && \rightarrow pK_1 = pK_2 \\ 3[\text{H}^+]_{0,5} &< [\text{H}^+]_{1,5} < 5,3[\text{H}^+]_{0,5} && \rightarrow pK_1 > pK_2 \\ [\text{H}^+]_{1,5} &= 3[\text{H}^+]_{0,5} && \rightarrow pK_1 \rightarrow +\infty \\ &&& pK_2 \rightarrow -\infty \\ &&& K_1 K_2 \neq 0, \text{ definiert.} \end{aligned}$$

Ist  $[\text{H}^+]_{1,5} < 3[\text{H}^+]_{0,5}$ , erhält man physikalisch-chemisch sinnlose Ergebnisse (negative Konstanten). Die Wurzel  $y_3$  liefert somit auch ein unbrauchbares Verhältnis  $[\text{H}^+]_{1,5}/[\text{H}^+]_{0,5}$  ( $K_1 = K_2$ , beide negativ), so daß die Mehrdeutigkeit der Bestimmungsgleichung (32) auf eine einzige physikalisch-chemisch sinnvolle Lösung reduziert wird.

Das Verhältnis  $[\text{H}^+]_{1,5} = 3[\text{H}^+]_{0,5}$  gibt die Grenze der stufenweisen Dissoziation an, da mit  $pK_2 \rightarrow -\infty$  eine Dissoziationszwischenstufe nicht existieren kann.

Schwarzenbach<sup>4</sup> errechnete unter der Voraussetzung der Nichtexistenz einer Zwischenstufe ( $[\text{HA}] = 0$ ) an seinem, von dem Bjerrum'schen verschiedenen Verfahren, die Grenze der stufenweisen Dissoziation ("2 Protonen in einem Schritt") und fand das gleiche Verhältnis der  $[\text{H}^+]$ -Konzentrationen wie oben.

Die sinnlosen Ergebnisse für  $[\text{H}^+]_{1,5} \leq 3[\text{H}^+]_{0,5}$  werden nicht durch ein bestimmtes Rechenverfahren bedingt, sondern ergeben sich aus einem Widerspruch in der Voraussetzung:  $[\text{H}^+]$  erniedrigt sich von  $\bar{n} = 1,5$  zu  $\bar{n} = 0,5$  auf ein Drittel. Die an den Liganden (Anion der Säure, Base . . .) gebundene Säuremenge  $C_S$  erniedrigt sich ebenfalls auf ein Drittel. Die Säure  $\text{H}_2\text{A}$  wird also in gleichem Maß neutralisiert wie die  $\text{H}^+$ -Ionen, was nur möglich ist, wenn sie vollständig dissoziiert ist. Das ist aber ein Widerspruch zur Voraussetzung  $\bar{n} \neq 0$ .

Für eine dreibasige Säure lautet das System der Bestimmungsgleichungen mit  $[\text{H}^+]_{2,5} = z$  und  $\bar{n}$ -Werten von 2,5; 1,5 und 0,5:

$$\begin{aligned} 0,5\beta_3 - 0,5x\beta_2 - 1,5x^2\beta_1 &= 2,5x^3 \\ 1,5\beta_3 + 0,5y\beta_2 - 0,5y^2\beta_1 &= 1,5y^3 \\ 2,5\beta_3 + 1,5z\beta_2 + 0,5z^2\beta_1 &= 0,5z^3 \end{aligned} \quad (33)$$

$$\left( \beta_n = \prod_{i=1}^n K_i \right)$$

Zur Berechnung der Differenz  $\text{pH}_{0,5} - \text{pH}_{2,5}$ , für die  $K_1 = K_2 = K_3 = K$  ist, kann man die erste oder die dritte Gleichung von (33) verwenden (2. Gleichung trivial). Aus der ersten Gleichung erhält man mit  $k = \sqrt{xz}$  und  $z/x = b$  eine Bestimmungsgleichung 3. Grades:

$$b^3 - 7b^2 - b - 25 = 0$$

deren reelle Wurzel  $b_1 = 7,55 \dots$  die pH-Differenz 0,878 ergibt, die mit der aus dem logarithmischen Iterationsverfahren errechneten identisch ist.

Zur Berechnung der Differenz  $\text{pH}_{0,5} - \text{pH}_{2,5}$ , für die die Konstanten das Vorzeichen wechseln, also physikalisch-chemisch sinnlose Werte annehmen, untersuchen wir den Vorzeichenwechsel der Determinanten.  $D$  und  $D_{\beta_3}$  sind immer positiv (da  $[\text{H}^+]$  immer positiv ist). Für  $D_{\beta_1}$  und  $D_{\beta_2}$  erhält man folgende Gleichungen:

$$D_{\beta_2} = \frac{1}{8}(45x^2y^3 + 3y^3z^2 + y^2z^3 - 25x^3y^2 - 15x^3z^2 - 9x^2z^3) \quad (34)$$

$$D_{\beta_1} = \frac{1}{8}(45x^3z + 3xz^3 + yz^3 - 25x^3y - 15xy^3 - 9y^3z)$$

Nehmen wir wieder an  $\text{pH}_{1,5} = (\text{pH}_{2,5} + \text{pH}_{0,5})/2$  ( $y = \sqrt{xz}$ ), werden Gl. (34), (35) für  $z = \sqrt[3]{25} \cdot x$  gleich Null. Dieses Verhältnis entspricht einer pH-Differenz  $\text{pH}_{0,5} - \text{pH}_{2,5} = 0,466$ .

#### *Schlußfolgerungen und Vergleich der nach beiden Verfahren erhaltenen Ergebnisse*

Die pH-Werte einer Titrationskurve einer mehrbasigen schwachen Säure und die pA-Werte einer Komplexbildungskurve bei  $\bar{n} = n - 0,5$  wurden als Kriterien für die Steilheit einer Kurve und die Abschätzung der zu erwartenden Werte verwendet. Dabei errechnet man für Säuretitrationskurven und für Komplexbildungskurven gleiche Zahlenwerte der pH- bzw. pA-Differenzen (an vergleichbaren Beispielen: zweibasige Säure, 1:2 Chelat usw.).

Aus dem logarithmischen Iterationsverfahren und aus der numerischen Berechnung erhält man gleiche Werte. Die pH-Differenz für die Gleichheit der pK-Werte ist für zweibasige Säuren  $\text{pH}_{0,5} - \text{pH}_{1,5} = 0,724$ , für dreibasige Säuren  $\text{pH}_{0,5} - \text{pH}_{2,5} = 0,878$ .

Werte unterhalb dieser Differenz führen zu Vertauschung der Reihenfolge der Konstanten. Man sollte aber immer erst prüfen, ob die Vertauschung nicht durch zu große Meßfehler der Titrationskurve hervorgerufen wird. Negative Konstanten errechnet man für eine pH-Differenz an zweibasigen Säuren für  $\text{pH}_{0,5} - \text{pH}_{1,5} < 0,477$ , an dreibasigen Säuren für  $\text{pH}_{0,5} - \text{pH}_{2,5} < 0,466$ . Diese Werte stimmen mit denen von Schwarzenbach für die Fälle "2 bzw. 3 Protonen in einem Schritt" gefundenen Werten überein.

Erhält man solche Werte, müssen Meßfehler vorliegen. Der Grenzwert der Konvergenz des Iterationsverfahrens fällt mit diesen Werten zusammen, d.h. das Iterationsverfahren ist für alle pH-Differenzen anwendbar, die noch positive Konstanten liefern. Damit wurde der von Schröder für die Berechnung der Stabilitätskonstanten von 1:2-Chelaten gefundene Grenzwert der Konvergenz bestätigt, der von van Uitert<sup>3</sup> angegebene Wert von  $\text{p}A_{0,5} - \text{p}A_{1,5} = 0,4343$  kann nicht richtig sein, da dieser schon in dem Bereich liegt, der zu physikalisch-chemisch sinnlosen Ergebnissen führt.

**Summary**—Two independent methods are described for calculation of protonation constants of tribasic ligands: the logarithmic iterative procedure as well as the numerical method is used for the estimation of the relative sequence of pK or log K values respectively from the pH differences at  $\bar{n} = 0,5, 1,5$  and  $2,5$  on the protonation curve. The convergence limits for the iterative procedure are given as a function of these pH differences. Closed expressions for the critical values of the iteration are presented for any pair of pH and  $\bar{n}$ .

**Résumé**—On décrit deux méthodes indépendantes pour le calcul des constantes de protonation de coordinats tribasiques: on emploie la technique itérative logarithmique aussi bien que la méthode numérique

pour l'estimation de la séquence relative des valeurs de  $pK$  ou  $\log K$  respectivement à partir des différences de  $pH$  à  $\bar{n} = 0,5$ ; 1,5 et 2,5 sur la courbe de protonation. Les limites de convergence pour la technique itérative sont données en fonction de ces différences de  $pH$ . On présente des expressions exactes pour les valeurs critiques de l'itération pour n'importe quelle paire de  $pH$  et  $\bar{n}$ .

## LITERATUR

1. J. K. Romary, D. L. Donnelly und A. C. Andrews, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1805.
2. I. G. Sayce, *Talanta*, 1968, **15**, 1397.
3. Le Grande, G. van Uitert, W. C. Fernelius und B. E. Douglas, *J. Am. Chem. Soc.*, 1953, **75**, 455
4. G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 947.
5. I. M. Bhatt, K. P. Soni und A. M. Trivedi, *Indian J. Chem.*, 1967, **5**, 165.
6. K. H. Schröder, *Acta Chem. Scand.*, 1966, **20**, 1401.
7. J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*. Haase, Copenhagen, 1941.
8. H. B. Jonassen, R. B. Le Blanc, A. W. Meibohm und R. M. Rogan, *J. Am. Chem. Soc.* 1950, **72**, 2430.

## CATION-EXCHANGE SEPARATION OF URANIUM FROM OTHER ELEMENTS IN TETRAHYDROFURAN-NITRIC ACID MEDIA CONTAINING TRIOCTYLPHOSPHINE OXIDE

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**Summary**—The batch distribution coefficients of Cu(II), Zn, Cd, Fe(III), Hg(II), Mg, Co(II), Ni, Pb, Ca and Bi were determined on the strongly acidic cation-exchange resin Dowex 50  $\times$  8 in 0.1M trioctylphosphine oxide in tetrahydrofuran–5% 12M nitric acid. In this mixture all these metal ions, except Bi, have high  $K_d$ -values and can be separated quantitatively from uranium which has a distribution coefficient of 0.1. Mixtures of U with Cu, Ni, Co, Cd or Fe were analysed to test the applicability of such separations. Different titrimetric and spectrophotometric methods were used to determine the elements subsequent to their separation from uranium on ion-exchange columns. The results show that accurate and effective separations can be achieved.

METHODS based upon the cation-exchange properties of uranium(VI) are seldom used to separate it from other elements, because cation-exchange resins show little selectivity towards the uranyl ion.<sup>1</sup> Thus, in pure aqueous nitric and hydrochloric acids, uranyl ions cannot be separated from numerous bivalent metal ions.<sup>2,3</sup> More suitable conditions prevail if sulphuric acid is used.<sup>4</sup>

The use of the principle known as combined ion-exchange–solvent extraction (CIESE) proposed by Korkisch,<sup>5</sup> greatly increases the selectivity of the cation-exchange procedures for uranium. Korkisch *et al.*<sup>6</sup> found that the  $\text{UO}_2(\text{II})$ -ion is easily separated from Th, Zr and Ce(III) in various solutions of 0.6M hydrochloric acid and aliphatic alcohols, acetic acid or tetrahydrofuran (THF). When the same organic solvents are used with nitric acid, there is considerable improvement in the separation<sup>6,7</sup> of uranium(VI) from virtually all elements except Mo(VI), V(V) and Bi. Of the various mixed systems the 90% THF–10% 12M nitric acid medium offers the best results.<sup>8</sup>

The use of organic extractants mixed with organic solvents and mineral acids has been found to be highly successful for several unique separations of metal ions on cation-exchange resins.<sup>9–12</sup> For instance, the alkali metals can be selectively separated from practically all other elements on Dowex 50 when 2-thenoyltrifluoroacetone in pyridine is used as eluent.<sup>9</sup> Another extractant that has proved to be extremely suitable is trioctylphosphine oxide. With this extractant dissolved in THF or methanol, in presence of hydrochloric or nitric acid, very effective separations of scandium from the rare earths,<sup>10</sup> and of hafnium plus zirconium,<sup>11</sup> and thorium from accompanying metal ions can be performed.<sup>12</sup>

In the present paper the applicability of trioctylphosphine oxide–THF–nitric acid systems for the separation of uranium from cadmium, cobalt, nickel, copper and iron on Dowex 50 was investigated, both titrimetric and spectrophotometric methods being used for the determination of the separated metal ions.

Thorium, zirconium and hafnium have very low  $K_d$  values in the systems used and are eluted with uranium, but scandium ( $K_d = 445$ ) can be separated from it.

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## EXPERIMENTAL

*Apparatus*

For the ion-exchange separations glass columns of 5 mm diameter and 0.25 m length were used.

*Reagents*

All chemicals used were of reagent-grade purity.

*Ion-exchange resin.* Air-dried Dowex 50 X 8 (100–200 mesh; hydrogen form) was used for the column separations and for the batch experiments. Before use the resin was purified by washing it successively with 6M nitric acid, distilled water and methanol, whereafter it was dried in air and stored in an amber bottle. For 1 kg of resin, 2 l. of 6M nitric acid, 5 l. of distilled water and 2 l. of methanol were used.

*Eluent solution.* Trioctylphosphine oxide (TOPO) (0.1M) in 95% tetrahydrofuran (THF)–5% 12M nitric acid (v/v) was freshly prepared for use.

*Metal ion solutions.* Solutions of Cu(II), Cd, Co(II), UO<sub>2</sub>(II), Ni, Fe(III), Ca, Zn, Mn(II), Mg, Pb, Bi and Hg(II) in 6M nitric acid were used, and standardized before use, by recommended procedures.

*Determination of distribution coefficients*

The batch distribution coefficients ( $K_d$  values) were determined by the technique described earlier.<sup>13</sup>

*Working procedure (Separation of metal ions from uranium)*

*Pretreatment of resin bed.* One gram of the resin is soaked for about 5 min in a few ml of the eluent solution and then the slurry is transferred to the ion-exchange column. The resulting resin bed is then washed with 5–10 ml of the eluent solution.

*Sorption and elution.* Nitric acid (6M, 0.5 ml) containing up to 500 mg of uranium plus the metal ion to be separated from it, is mixed with 4.5 ml of the eluent solution and the resulting mixture is passed through the pretreated resin bed at a flow-rate corresponding to the back-pressure of the resin column. The addition of the 0.5 ml of acid was found necessary to increase the solubility of the metal ions in this medium. Under these conditions the metal ions are strongly retained on the resin while most of the uranium is eluted. The uranium is completely eluted by passage of 20–60 ml of the eluent solution, according to the concentration of uranium present. The column is then washed to remove TOPO, using 10 ml of a mixture consisting of 95% THF and 5% 12M nitric acid (v/v). Subsequently the adsorbed element is eluted with 15 ml of 6M hydrochloric acid.

*Quantitative determination of the metal ions*

*Titrimetric determinations.* For macro amounts of the elements, EDTA titrations, with suitable indicators, were used. The solution of the metal in 6M hydrochloric acid was evaporated to dryness, the residue was dissolved in water and the pH was adjusted to the desired value and the metal ion was titrated with standard EDTA solution. The indicators used were Eriochrome Black T, Xylenol Orange, Murexide, Pyrocatechol Violet and sulphosalicylic acid.

*Spectrophotometric determinations.* For determining microgram amounts of the metals well-known spectrophotometric procedures were used.

Cadmium was determined with Xylenol Orange at pH 6.3 (hexamine–nitric acid buffer), the absorbance being measured at 575 nm against a reagent blank. Beer's law is obeyed in the range 2–12  $\mu\text{g Cd/ml}$ .<sup>14</sup>

Cobalt was determined with nitroso-R-salt at pH 6 (sodium acetate buffer) against a reagent blank at 500 nm. Beer's law is obeyed in the range 0.1–1  $\mu\text{g Co/ml}$ .<sup>15</sup>

Iron was determined with 1,10-phenanthroline in the presence of hydroxylamine hydrochloride at pH 3.6 (ammonium acetate–acetic acid buffer). The absorbance was measured against water at 508 nm. Beer's law is obeyed in the range 1–10  $\mu\text{g Fe/ml}$ .<sup>16</sup>

Nickel was determined with dimethylglyoxime at pH 9 (ammonium acetate–ammonia buffer) and extraction of the complex into chloroform. The absorbance was measured at 375 nm against chloroform. Beer's law is obeyed in the range of 1–10  $\mu\text{g Ni/ml}$ .<sup>16</sup>

Copper was determined as the diethyldithiocarbamate complex at pH 9 by extraction of the complex into butyl acetate. The absorbance was measured at 440 nm. Beer's law is obeyed in the range 0.1–1  $\mu\text{g Cu/ml}$ .<sup>16</sup>

In all these spectrophotometric determinations the metal ion solutions in 6M hydrochloric acid (eluates) were evaporated to dryness before the determinations were performed. Calibration curves were prepared from standard metal ion solutions treated exactly as the unknown solutions.

## RESULTS AND DISCUSSION

The distribution coefficients of Cd, Zn, Co, Fe, Ca, Mg, Ni, Cu, Pb, Bi and Hg in 0.1M TOPO–95% THF–5% 12M nitric acid are recorded in Table I. The  $K_d$  value for uranium<sup>12</sup> is also listed for comparison.



TABLE I.—DISTRIBUTION COEFFICIENTS OF VARIOUS METAL IONS

| Metal ion            | $K_d$ | Metal ion | $K_d$ |
|----------------------|-------|-----------|-------|
| UO <sub>2</sub> (II) | 0.1   | Ca        | 9620  |
| Cd                   | 3190  | Mg        | 520   |
| Zn                   | 3480  | Ni        | 5880  |
| Co(II)               | 4730  | Cu(II)    | 1360  |
| Fe(III)              | 5680  | Hg(II)    | 1210  |
| Bi                   | 68    | Pb        | 484   |

From the  $K_d$  values it is obvious that uranium can be effectively separated from the elements having high  $K_d$ -values, *i.e.*, Cd, Zn, Co, Fe, Cu, Ni, Ca, Mg, Pb and Hg. The results showing the separation of amounts from milligrams down to a few  $\mu\text{g}$  of Cu, Ni, Co, Cd and Fe, taken as representatives for this method, are shown in Tables II and III. The concentration of uranium was always much higher than that of the metal ion, sometimes 5000 times as much. In separation of uranium from Fe, Co, Ni or Cu, in mg amounts, a coloured zone due to the adsorbed metal is formed at the top of the column. This zone does not move down the resin bed to any appreciable extent during elution and washing.

From the results shown in Table II it is obvious that milligram amounts of the metals can be titrated quantitatively with EDTA. However, the error is somewhat high for submilligram amounts. This can be overcome by using spectrophotometric determinations which show high accuracy as seen from Table III.

TABLE II.—SEPARATION OF *mg*-AMOUNTS OF METAL IONS FROM URANIUM

| Uranium taken,<br><i>mg</i> | Metal taken,<br><i>mg</i> | Metal found,<br><i>mg</i> |
|-----------------------------|---------------------------|---------------------------|
| 500                         | 4.45 Cu                   | 4.51 Cu                   |
| 100                         | 0.102 Cu                  | 0.106 Cu                  |
| 500                         | 4.34 Ni                   | 4.29 Ni                   |
| 100                         | 0.100 Ni                  | 0.104 Ni                  |
| 500                         | 5.473 Fe                  | 5.53 Fe                   |
| 100                         | 0.508 Fe                  | 0.502 Fe                  |
| 500                         | 10.00 Cd                  | 9.96 Cd                   |
| 100                         | 5.00 Cd                   | 5.05 Cd                   |
| 50                          | 0.25 Cd                   | 0.26 Cd                   |
| 500                         | 5.00 Co                   | 4.83 Co                   |
| 100                         | 0.500 Co                  | 0.518 Co                  |

TABLE III.—SEPARATION OF  $\mu\text{g}$ -AMOUNTS OF METAL IONS FROM URANIUM

| Uranium taken,<br><i>mg</i> | Metal taken,<br>$\mu\text{g}$ | Metal found<br>$\mu\text{g}$ |
|-----------------------------|-------------------------------|------------------------------|
| 50                          | 10.0 Cu                       | 10.7 Cu                      |
| 25                          | 5.0 Cu                        | 5.3 Cu                       |
| 50                          | 25.0 Ni                       | 27.0 Ni                      |
| 25                          | 5.0 Ni                        | 5.4 Ni                       |
| 50                          | 10.0 Fe                       | 10.4 Fe                      |
| 25                          | 5.0 Fe                        | 5.5 Fe                       |
| 50                          | 45.0 Cd                       | 45.0 Cd                      |
| 25                          | 25.0 Cd                       | 28.0 Cd                      |
| 50                          | 10.0 Co                       | 10.3 Co                      |
| 25                          | 5.0 Co                        | 5.05 Co                      |

The results listed in Table III show that even a few  $\mu\text{g}$  of the bivalent and trivalent metals can be separated quantitatively from uranium. Consequently this technique is well suited for purification of uranyl nitrate and to enrich these strongly adsorbed elements before their determination. Analysis by means of this method offers the possibility of rapidly determining impurities in uranyl nitrate solutions especially if their content is low.

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**Zusammenfassung**—Die Verteilungskoeffizienten (im Einzelansatz) von Cu(II), Zn, Cd, Fe(III), Hg(II), Mg, Co(II), Ni, Pb, Ca und Bi an dem stark sauren Kationenaustauschharz Dowex 50  $\times$  8 wurden gegen 0,1M Triäthylphosphinoxid in Tetrahydrofuran—5% 12M Salpetersäure bestimmt. In diesen Gemisch haben alle genannten Metallionen außer Bi hohe  $K_d$ -Werte und können quantitativ von Uran getrennt werden, das einen Verteilungskoeffizienten von 0,1 hat. Gemische von U mit Cu, Ni, Co, Cd oder Fe wurden analysiert, um die Anwendbarkeit solcher Trennungen zu überprüfen. Es wurden verschiedene titrimetrische und spektrophotometrische Methoden verwendet, um die Elemente nach ihrer Abtrennung von Uran an Ionenaustauschsäulen zu bestimmen. Die Ergebnisse zeigen, daß genaue und effektive Trennungen erzielt werden können.

**Résumé**—On a déterminé les coefficients de partage de Cu(II), Zn, Cd, Fe(III), Hg(II), Mg, Co(II), Ni, Pb, Ca et Bi sur la résine échangeuse de cations fortement acide Dowex 50  $\times$  8 dans l'oxyde de triéthylphosphine 0,1M en tétrahydrofuran—5% d'acide nitrique 12M. Dans ce mélange, tous ces ions métalliques, à l'exception de Bi, ont des valeurs  $K_d$  élevées et peuvent être séparés quantitativement de l'uranium qui a un coefficient de partage de 0,1. On a analysé des mélanges d'U avec Cu, Ni, Co, Cd ou Fe pour éprouver les possibilités d'application de telles séparations. On a utilisé différentes méthodes titrimétriques et spectrophotométriques pour déterminer les éléments après leur séparation de l'uranium sur colonnes échangeuses d'ions. Les résultats montrent que l'on peut réaliser des séparations précises et efficaces.

#### REFERENCES

1. Z. Hagiwara and K. Ochiai, *J. Nucl. Sci. Technol. Tokyo*, 1968, **5**, 104.
2. K. A. Kraus, F. L. Moore and F. Nelson, *J. Am. Chem. Soc.*, 1956, **78**, 2692.
3. F. W. E. Strelow, *Anal. Chem.*, 1960, **32**, 1185.
4. F. W. E. Strelow, R. Rethenmeyer and C. J. C. Bothna, *ibid.*, 1965, **37**, 106.
5. J. Korkisch, *Separation Science*, 1966, **1**, 159.
6. J. Korkisch, F. Feik and S. S. Ahluwalia, *Talanta*, 1967, **14**, 1069.
7. J. Korkisch and S. S. Ahluwalia, *Anal. Chem.*, 1966, **38**, 497.
8. J. R. Musich, K. A. Orlandini and J. Korkisch, *U.S. At. Energy Comm. Rept.*, ANL-7401, January 1968.
9. J. Korkisch and K. A. Orlandini, *Anal. Chem.*, 1968, **40**, 1127.
10. K. A. Orlandini and J. Korkisch, *Separation Science*, 1968, **3**, 255.
11. J. Korkisch and K. A. Orlandini, *Talanta*, 1969, **16**, 45.
12. *Idem*, *Anal. Chem.*, 1968, **40**, 1952.
13. K. A. Orlandini and J. Korkisch, *U.S. At. Energy Comm. Rept.*, ANL-7415, January 1968.
14. M. Otomo, *Bull. Chem. Soc. Japan*, 1964, **37**, 504.
15. T. C. J. Ovenston and C. A. Parker, *Anal. Chim. Acta*, 1950, **4**, 142.
16. T. Takeuchi, M. Suzuki, D. Ishii, K. Saito, I. Fujishima, T. Fukasawa, T. Tanaka and T. Yoshimori, *Mem. Fac. Eng. Nagoya Univ.*, **15**(1), May 1963.

## DETERMINATION OF INDIUM AND THALLIUM IN INDIUM-THALLIUM ALLOYS\*

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**Summary**—The thallium-indium alloys were dissolved in sulphuric acid (1 + 1). In this medium thallium remained in the univalent state and could be determined directly, without a separation, by an oxidation-reduction titration with potassium bromate. The indium was determined directly with an EDTA titration. Ascorbic acid was added to maintain the thallium in the univalent state, which did not interfere. Ascorbic acid also masked any interfering trivalent thallium by effectively reducing it to the univalent state. Sharp end-points were obtained for both titrations, which were carried out in the temperature range of 50–95°. The method offers excellent precision and accuracy.

A RAPID METHOD was sought, which would give high accuracy without a separation, for the determination of indium and thallium in thallium-indium alloys used in phase diagram studies in this laboratory. In searching for a suitable thallium determination both oxidation-reduction<sup>1</sup> and chelometric methods using EDTA as the titrant were reviewed and tested on mixtures simulating the alloys to be analysed. Direct titrations of trivalent thallium with EDTA may be carried out at pH 4–5 in a hot solution, using Xylenol Orange<sup>2–5</sup> as the indicator, at pH 10 with Eriochrome Black T, and at pH 4–6 with sodium azide as indicator.<sup>6</sup> Back titrations of excess of EDTA<sup>3,4</sup> with bismuth, thorium, and cobalt have also been used. Masking the indium or separating it from the thallium prior to an EDTA titration proved to be necessary. The bromate oxidation-reduction titration<sup>7–10</sup> was chosen for the thallium determination rather than the EDTA titration because it gave the high accuracy desired, without a separation.

Numerous chelometric titrations of indium are reported in the literature. The titrimetric determination of indium with EDTA as the titrant and Xylenol Orange as the indicator<sup>3,11,12</sup> was chosen because it was simple and rapid and gave the desired accuracy. The proper conditions for the titration, including the acid concentration, the method of masking the thallium, and the effect of the salt concentration and temperature are discussed.

### EXPERIMENTAL

#### Reagents

*Standard indium solution.* Pure indium metal (99.999% purity), 1 g, was dissolved in dilute hydrochloric acid. The solution was transferred to a weight burette, diluted to approximately 60 ml, and weighed.

*Standard thallium solution.* Pure thallium metal, 4 g, was weighed, placed in a 250-ml beaker, covered with 50 ml of sulphuric acid (1 + 1) and heated strongly to effect solution. The solution was transferred to a weight burette, cautiously diluted to approximately 60 ml, and weighed.

*EDTA solution, 0.05M.* The disodium salt of EDTA, 70 g, was dissolved in 500 ml of water

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which contained 2-3 g of sodium hydroxide. When a clear solution was obtained the pH was adjusted to 6 with hydrochloric acid and the solution was diluted to 4 l. with water. The solution was standardized against the standard indium solution, using the procedure which is described below for the determination of indium.

*Potassium bromate solution, 0.1N.* Reagent grade potassium bromate, 11.1 g, was dissolved in 4 l. of water and mixed thoroughly. The potassium bromate was standardized against primary standard arsenious oxide. Naphthol Blue-Black was used as the indicator.

*Acetate buffer solution, 1.0M.* Ammonium acetate, 78 g, was dissolved in water and diluted to 1 litre.

*Xylenol Orange indicator solution 0.25%.*

*Methyl Orange indicator solution, 0.01%.*

#### *Dissolution*

Indium-thallium alloys (1.0-1.5 g samples) containing up to 96% thallium were weighed, placed in 400-ml beakers, and covered with sulphuric acid (1 + 1). The solutions were heated to dissolve the alloy.

#### *Thallium titration*

An aliquot of the sample, containing 200-400 mg of thallium(I) and preferably 3 or 4 ml of concentrated sulphuric acid was transferred to a 250-ml beaker. The aliquot was diluted to 150 ml and placed on a hot-plate/stirrer. With the hot-plate/stirrer temperature adjusted to medium high the solution reached the desired temperature range (50-95°) for titration in several minutes. The proper acidity was reached by adding 10 ml. of concentrated hydrochloric acid. Two drops of Methyl Orange indicator were added at the start of the titration. The standard potassium bromate was added from a 50-ml burette and as the end-point was approached an additional two drops of indicator were added. A very sharp colour change from yellow-orange to colourless was observed. An indicator blank correction was made.

#### *Indium titration*

An aliquot containing 30-75 mg of indium was taken in a 250-ml beaker for the indium determination. The volume was adjusted to 50 ml with distilled water. During stirring and heating of the solution to 50-95° on the hot-plate/stirrer, 500 mg of fresh ascorbic acid were added. Ascorbic acid loses its effectiveness and appears to decompose even in unopened bottles. Then 15-20 ml of the acetate buffer solution were added to the indium solution and the volume was adjusted to about 150 ml. The pH was adjusted to 3.5 with dilute sulphuric acid or dilute ammonia solution and controlled to  $\pm 0.15$  pH unit at the end-point. The titration was carried out with 0.05M EDTA, with Xylenol Orange as the indicator. A sharp red to yellow colour change was observed.

## RESULTS AND DISCUSSION

The results of standardizations and final procedures are reported below. Useful notes and observations during development are discussed.

Standardization of the potassium bromate was done against primary standard arsenious oxide. Approximately 40 ml of potassium bromate were required for titration of 200-220 mg of the arsenious oxide. The standard deviation for five weighed portions was  $\pm 0.000022$  for a 0.1039N solution.

TABLE I.—DETERMINATION OF THALLIUM IN THE PRESENCE OF INDIUM

| Thallium taken,<br>mg | Thallium recovered,<br>mg | Indium present,<br>mg | Recovery, % |
|-----------------------|---------------------------|-----------------------|-------------|
| 365.5                 | 365.6                     | none                  | 100.0       |
| 280.1                 | 280.1                     | none                  | 100.0       |
| 362.7                 | 362.7                     | none                  | 100.0       |
| 403.2                 | 403.1                     | 217.9                 | 100.0       |
| 325.3                 | 325.5                     | 326.8                 | 100.1       |
| 371.9                 | 372.1                     | 108.9                 | 100.1       |

*Thallium determination*

Table I illustrates results obtained upon titrating thallium (I) with potassium bromate. A standard deviation of 0.129 mg was obtained for these titrations.

The effect of the presence of increased amounts of sulphuric acid was tested. As much as 18 ml of sulphuric acid introduced into the titration solution caused no undesirable effect.

In order to prevent precipitation of thallium(I) chloride, the acidity of the solution to be titrated was adjusted with hydrochloric acid after the solution had reached the titration temperature. The thallium(I) chloride still had a tendency to precipitate when 400 mg or more were present and the sulphuric acid concentration was 1*N* or less. This caused no difficulty when proceeding as recommended in the titration procedure, and upon addition of 50–75% of the required bromate, the thallium titration solution cleared and a normal end-point was obtained.

Methyl Orange, an irreversible indicator, was added near the end-point once the approximate end-point had been established. The end-point of the first titration of each unknown solution was accurately verified by back-titrating the titrated solution with indicator solution from an eye-dropper. The titre of the indicator was established by titrating a blank solution containing 20 drops of indicator to the end-point with potassium bromate. When a slight over-shooting of the end-point occurred, a quick and accurate correction was also made by using this method.

The range of temperature for both the thallium and indium titrations was established to be 50–90°. A temperature of 50° or above was needed to promote the speed of the reaction and sharpen the end-point. The disadvantage of boiling the sample was that vigorous bubbling obscured the colour change.

*Indium determination*

Table II illustrates the results obtained when titrating indium in the presence of thallium. Any trivalent thallium was masked by reducing it to the univalent state with ascorbic acid. In the univalent state the thallium does not interfere. A standard deviation of 0.037 mg was obtained.

TABLE II.—DETERMINATION OF INDIUM IN THE PRESENCE OF THALLIUM

| Indium taken,<br><i>mg</i> | Indium recovered,<br><i>mg</i> | Thallium present,<br><i>mg</i> | Recovery, % |
|----------------------------|--------------------------------|--------------------------------|-------------|
| 66.17                      | 66.15                          | none                           | 99.97       |
| 46.42                      | 46.40                          | none                           | 99.96       |
| 40.02                      | 40.05                          | none                           | 100.08      |
| 52.31                      | 52.25                          | none                           | 99.89       |
| 60.45                      | 60.39                          | 221.9*                         | 99.90       |
| 60.86                      | 60.90                          | 443.8*                         | 100.07      |
| 47.47                      | 47.51                          | none                           | 100.08      |
| 60.04                      | 60.06                          | 387.2*                         | 100.03      |
| 53.44                      | 53.44                          | none                           | 100.01      |
| 17.12                      | 17.15                          | 321.1†                         | 100.19      |

\* Thallium added as Tl<sup>3+</sup>.

† Thallium added as Tl<sup>+</sup>.

A range of 30–70 mg of indium per titration was suggested for convenience when using a 10-ml burette. In practice a range of up to 120 mg caused no titration difficulty.

High salt content in the indium titration affected the sharpness of the end-point. If a very large amount of acid was used in dissolution, removal of the large excess of acid by fuming off prior to the neutralization helped in obtaining a sharper end-point.

### *Dissolutions*

The ease and speed of dissolution in sulphuric acid varied considerably as the composition of the alloy ranged thallium-rich to indium-rich. Dissolution of the samples with high indium content (>85%) is slow. Dissolution of high thallium content alloys (>85%) was speeded up by heating the solutions till strong fumes of sulphur trioxide were evolved. However, extremely strong fuming with sulphuric acid may cause the precipitation of some free sulphur. It is desirable to avoid heating the solution to this extent, to avoid clouding the solution.

If only indium is to be determined, the rate of dissolution can be increased by using *aqua regia* rather than sulphuric acid. The presence of up to 9 ml of *aqua regia* introduced into the indium titration solution caused no apparent problem in masking the thallium or in the indium titration, but it is normally desirable to keep the acid concentration as low as possible for the sharpest end-point. The advantages of the rapid dissolution by this method disappear if the thallium is also to be determined. The thallium must then be reduced to the univalent state with sulphur dioxide, after the removal of the nitric acid by fuming with sulphuric acid. The excess of sulphur dioxide is removed by boiling and passing a stream of carbon dioxide through the solution. The thallium can then be titrated as indicated above.

**Zusammenfassung**—Die Thallium-Indium-Legierungen wurden in Schwefelsäure (1 + 1) gelöst. In diesem Medium verblieb Thallium im einwertigen Zustand und konnte direkt ohne Abtrennung durch Redox-titration mit Kaliumbromat bestimmt werden. Das Indium wurde direkt mit einer EDTA-Titration bestimmt. Ascorbinsäure wurde zugegeben, um Thallium im nicht störenden einwertigen Zustand zu halten. Ascorbinsäure maskierte auch jedes störende dreiwertige Thallium durch effektive Reduktion zum einwertigen Zustand. Scharfe Endpunkte wurden bei beiden Titrationen erhalten; beide wurden bei 50–95° ausgeführt. Das Verfahren bietet ausgezeichnete Genauigkeit und Richtigkeit.

**Résumé**—On a dissous les alliages thallium-indium en acide sulfurique (1 + 1). Dans ce milieu, le thallium reste à l'état monovalent et peut être dosé directement, sans séparation, par un titrage d'oxydo-réduction au moyen de bromate de potassium. L'indium est déterminé directement par un titrage à l'EDTA. On ajoute de l'acide ascorbique pour maintenir le thallium à l'état monovalent, qui ne gêne pas. L'acide ascorbique dissimule aussi tout thallium trivalent gênant en le réduisant efficacement à l'état monovalent. On a obtenu des points de fin de dosage nets pour les deux titrages, qui ont été menés dans le domaine de température 50–95°. La méthode offre une précision et une fidélité excellentes.

### REFERENCES

1. E. H. Swift and C. S. Garner, *J. Am. Chem. Soc.*, 1936, **58**, 113.
2. H. Flaschka, A. J. Barnard Jr., and W. C. Broad, *Chemist-Analyst*, 1958, **47**, 78.
3. *Idem, ibid.*, 1958, **47**, 52.
4. A. J. Barnard, Jr., W. C. Broad and H. Flaschka, *The EDTA Titration*, J. T. Baker, Phillipsburg, N. J., 1957.
5. J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1957, **46**, 92.
6. T. N. Srivastava and N. Singh, *Z. Anal. Chem.*, 1966, **218**, 261.

7. I. M. Kolthoff, *Rec. Trav. Chim.*, 1922, **41**, 172.
8. E. Zintl and G. Rienacker, *Z. Anorg. Allgem. Chem.*, 1926, **153**, 276.
9. I. M. Koreman, *Analytical Chemistry of Thallium*, p. 78. Israel Program for Scientific Translations, Jerusalem, 1963.
10. M. N. Chepik, *Sb. Nauchn. Tr. Vses. Nauchn.-Issled. Gorno-Met. Inst. Tsvet. Metal.*, 1959, **5**, 81.
11. M. Kapanica and R. Přibil, *Collection Czech. Chem. Commun.*, 1960, **25**, 2230.
12. A. I. Busev, *The Analytical Chemistry of Indium* (transl. J. T. Greaves), p. 288. Pergamon, Oxford, 1962.

# MICRODOSAGE DU CARBONE DANS LES COMPOSÉS ORGANIQUES PAR COMBUSTION QUASI-INSTANTANÉE ET TITRAGE COULOMETRIQUE AUTOMATIQUE DU DIOXYDE DE CARBONE

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**Résumé**—Les auteurs décrivent une méthode simple et rapide de microdosage du carbone dans les composés organiques. Le prélèvement analytique (1–3 mg) est minéralisé par combustion quasi-instantanée, dans une chambre vide à 950–1050°, sous un courant d'oxygène de 80–100 ml.mn<sup>-1</sup>. Cette combustion dynamique dans l'oxygène, doit être complétée par passage des gaz sur une garniture d'oxyde de cuivre à 850°. Les produits de combustion halogénés et soufrés sont retenus par une garniture d'alumine argentée à 750–800°. L'eau et les oxydes acides de l'azote sont respectivement retenus à la température ambiante par du perchlorate de magnésium (anhydron) et du dioxyde de manganèse. Le dioxyde de carbone est absorbé dans le compartiment cathodique de la cellule d'un coulomètre automatique avec formation d'ions H<sup>+</sup> qui sont neutralisés par des ions OH<sup>-</sup> engendrés par électrolyse. Cette méthode permet le microdosage du carbone dans les composés organiques contenant des halogènes (dont le fluor), du phosphore et des métaux. Cependant quelques composés organiques dont les molécules comportent des noyaux polynucléaires conduisent à des résultats erronés par défaut; il est alors nécessaire d'ajouter un réactif donneur d'oxygène au prélèvement analytique afin d'obtenir une combustion complète. Dans les conditions opératoires du présent travail, l'hémipentaoxyde de vanadium semble le meilleur d'entre eux. Les prélèvements analytiques solides sont pesés et analysés dans des nacelles de platine ou de porcelaine. Les liquides sont pesés dans des ampoules de verre "Pyrex" qui sont ensuite posées dans des nacelles de platine et recouvertes par un petit morceau de toile de platine. Dans le cas des liquides stables l'un des capillaires de l'ampoule est brisé avant son introduction dans le tube à combustion mais dans le cas de liquides volatils l'ampoule scellée est introduite telle quelle dans la chambre de combustion où elle explose. La précision obtenue est supérieure à celle des méthodes classiques.

LA CROISSANCE et la diversification de la demande de microanalyses organiques ont orienté les recherches de notre Service vers la mise au point de méthodes automatiques permettant de doser simultanément plusieurs éléments sur un même prélèvement analytique. Toutefois, le pesage du prélèvement microanalytique reste une opération singulière qui s'oppose, le plus souvent, à l'automatisation complète des méthodes étudiées. C'est pourquoi, à l'instar de Reitsem et Allphin<sup>1</sup> l'idée de supprimer le pesage des prélèvements nous a conduits à examiner diverses méthodes susceptibles de permettre la détermination de rapports tels que (N)/(C), (H)/(C), (S)/(C) *etc.* . . \* des éléments présents dans les composés organiques soumis à l'analyse. La connaissance des teneurs absolues de chacun de ces éléments peut, cependant, demeurer nécessaire;

\* La parenthèse indique qu'il s'agit d'une masse ou d'un nombre de moles de carbone, d'azote, d'hydrogène, de soufre *etc.*



il convient, *dans ce cas*, d'adjoindre aux postes de microanalyse fournissant lesdits rapports, un poste complémentaire permettant le dosage, avec une précision aussi élevée que possible, de l'un des précédents éléments, le carbone, par exemple, qui pour la matière organique est généralement le plus important.

L'objet du présent travail est de décrire une méthode automatique de microdosage précis du carbone. D'une façon générale, l'étude d'une méthode automatique de dosage, en microanalyse organique élémentaire, implique un double choix: celui de l'espèce moléculaire représentative de l'élément à doser, produite par la minéralisation et objet de la mesure et celui de la méthode de mesurage. Le dioxyde de carbone, qui est produit par une minéralisation aisée, la combustion du prélèvement analytique du composé organique dans un excès d'oxygène, est choisi comme molécule représentative du carbone. Il présente, entre autres avantages, celui de se prêter très facilement à son propre transfert depuis le site de combustion à celui de mesurage. En vue de l'automatisation, il convient d'ailleurs, au mieux, d'effectuer ce dernier sur une grandeur physique dont la variation soit proportionnelle à la quantité de dioxyde de carbone à doser et réponde aux impératifs simultanés d'une grande précision, d'une sensibilité suffisante et de spécificité.

Les grandeurs physiques susceptibles de permettre le mesurage du dioxyde de carbone ont été passées en revue par Levy.<sup>2</sup> Parmi les méthodes de mesurage décrites l'acidimétrie coulométrique paraît l'une des plus appropriées d'autant plus qu'un appareil initialement fondé sur les travaux de Oelsen, Abresch, Graue et Fahrion, cités par Abresch et Claassen,<sup>3</sup> sur le dosage du carbone dans les aciers et commercialisé par Schoeps a déjà fait ses preuves dans le domaine de la microanalyse. C'est ainsi que Fraisse et Levy<sup>4</sup> l'utilisent dans une méthode de microdosage de l'oxygène impliquant un titrage coulométrique du dioxyde de carbone. Martin, Floret et Lemaitre<sup>5</sup> dosaient déjà avec cet appareil le carbone et l'hydrogène par titrages de quantités de dioxyde de carbone proportionnelles à celles de chacun de ces éléments. Mais l'objectif que nous visons exige une précision supérieure à celle qu'obtiennent ces derniers auteurs pour le dosage du carbone. Ils ne dosent en effet qu'une fraction du dioxyde de carbone issu de la combustion du prélèvement analytique, grâce à l'emploi d'une pompe diviseuse rejetant les 9/10 des gaz de combustion; il en résulte une multiplication des erreurs expérimentales par un facteur 10, ce qui est évidemment défavorable. Notre méthode comporte, au contraire la mesure de la totalité du dioxyde de carbone et fournit des résultats plus précis du dosage du carbone.

#### PRINCIPE

Le prélèvement analytique est brûlé quasi-instantanément dans un grand excès d'oxygène pur à 950–1000° suivant une technique voisine de celle décrite par Ingram.<sup>6</sup> Elle en diffère par le fait que la combustion n'est pas statique, comme la sienne, mais dynamique, c'est à dire qu'elle a lieu sous courant d'oxygène. Ce dernier, (d'un débit d'environ 100 ml. mn<sup>-1</sup>) entraîne les gaz de combustion sur une garniture d'oxyde de cuivre en fil maintenue à 800–850°, puis sur une garniture d'alumine argentée<sup>7</sup> à environ 750–800° et un tampon de laine d'argent retenant les produits de combustion du soufre et des halogènes. L'eau formée est fixée, à température ambiante, sur du perchlorate de magnésium et les oxydes de l'azote sur du dioxyde de manganèse. Le dioxyde de carbone ainsi débarrassé des gaz gênants est entraîné dans le compartiment cathodique de la cellule d'électrolyse du coulomètre.

Rappelons qu'il y réagit sur une solution de perchlorate de baryum en engendrant des ions  $H^+$  qui sont neutralisés par les ions  $OH^-$  produits par l'électrolyse de l'eau. Le coulomètre (*cf.* notice du constructeur) délivre un courant d'électrolyse haché fourni, sous forme de quantités égales d'électricité, par les décharges successives des condensateurs auxquelles correspondent des impulsions commandant un compteur numérique; la quantité totale d'électricité utilisée lors d'un titrage est proportionnelle au nombre total d'impulsions correspondantes lu sur le compteur. La fréquence des décharges est automatiquement réglée par la variation du pH de la solution, elle atteint une valeur maximale de 12,5 impulsions par seconde puis décroît progressivement pour n'être plus que de 0,5 impulsion par seconde à l'approche du point final de titrage. Le fonctionnement et l'arrêt de l'électrolyseur sont commandés automatiquement par un dispositif asservi au pH de la solution.

## PARTIE EXPERIMENTALE

### Appareillage

*Purification de l'oxygène.* L'oxygène issu d'un tube de gaz comprimé, pourvu d'un manodétendeur traverse, en premier lieu, un régulateur de pression constitué par un tube en T plongeant, à profondeur réglable, dans une éprouvette remplie d'huile de vaseline pure à travers laquelle l'excès de gaz s'échappe dans l'atmosphère. L'oxygène traverse ensuite une vanne électromagnétique (*cf.* Fig. 1) dont la fonction est décrite et discutée ci-après et est dirigé vers un rotamètre (1, Fig. 1) préalablement étalonné; son débit est fixé entre 80 et 100 ml.  $mn^{-1}$ . Il est ensuite purifié sur une garniture d'oxyde de cuivre en fil portée à 750° dans un four électrique tubulaire<sup>8</sup> suivi d'un tube absorbeur (3, Fig. 1) comportant une garniture d'amiante sodé (ascarite) et de perchlorate de magnésium (anhydron).

*Tube à combustion.* Le tube à combustion (Fig. 2) est en silice transparente, de qualité étirée; il comprend la chambre de combustion (A, Fig. 2), une partie tubulaire (B, Fig. 2) dont l'axe parallèle à celui de la chambre est décalé vers le bas, elle est pourvue d'un ajustage latéral; ces deux parties sont identiques à celles décrites par Ingram.<sup>6</sup>

La chambre de combustion est prolongée par un tube (C, Fig. 2) destiné à recevoir l'oxyde de cuivre (3, Fig. 2) et les réactifs de rétention des composés de combustion gênants (1 et 2, Fig. 2); il est terminé par un tube capillaire abducteur pourvu d'un joint rodé mâle RIN 00. La partie du tube contenant les réactifs est placée dans un four classique de microanalyse de 160 mm de longueur<sup>8</sup> maintenu en son centre à la température de 800° et alimenté sous une tension de 40 V qui permet d'y faire passer un courant d'intensité voisine de 2,5-3 A.

Le tube à combustion est complété par un système d'introduction (*cf.* Fig. 2) de la nacelle dans la chambre de combustion, constitué par un fil de platine iridié, en hélice, scellé à l'une des extrémités d'une baguette de silice et pourvu d'un barreau aimanté incorporé à l'autre extrémité (*cf.* Ingram<sup>6</sup>).

*Four à combustion.* Le four tubulaire est constitué par un tube laboratoire en mullite de 120 mm de longueur et 40 mm de diamètre intérieur porteur d'un bobinage de fil de Kanthal A<sub>1</sub> de 1,25 mm de diamètre, comportant 17 spires dont 8 spires ressérées à chacune des extrémités, noyé dans un ciment réfractaire. Le tube laboratoire est centré par deux flasques latérales en acier inoxydable, de 200 mm de diamètre, au sein d'une masse isolante de fibre d'amiante contenue dans une carcasse métallique cylindrique d'acier inoxydable. La résistance chauffante du four est alimentée sous une tension d'environ 40 V qui permet d'y faire passer un courant d'intensité voisine de 9,5-10 A en vue d'atteindre une température de 1000° en son centre.

Les températures du four à combustion et du four à réactifs sont repérées lorsqu'ils sont accolés et tous deux sous tension à l'aide d'un thermo couple platine-platine rhodié à 10%.

*Rétention de l'eau et des oxydes acides de l'azote.* A la sortie du tube à combustion l'eau est piégée sur une garniture de perchlorate de magnésium placée dans un tube en verre "Pyrex" (5, Fig. 1). Les gaz traversent ensuite une boule en verre d'un volume de 50 ml (6, Fig. 1); celle-ci permet à la fois la dilution du dioxyde de carbone, pour éviter la saturation de la cellule de titrage coulométrique, et des oxydes acides de l'azote pour permettre (par oxydation de NO en N<sub>2</sub>O<sub>4</sub>) leur rétention sur le dioxyde de manganèse qui est placé, immédiatement à sa sortie, dans un tube en U (7, Fig. 1).

*Mesurage.* L'appareil utilisé est le coulomètre Schoeps\* type CTA 5 C. Seules la partie électronique et la cellule électrochimique du coulomètre sont utilisées dans notre méthode; la

\* Fournisseur: Schoeps, 41 Duisburg Beck, République Fédérale Allemagne.

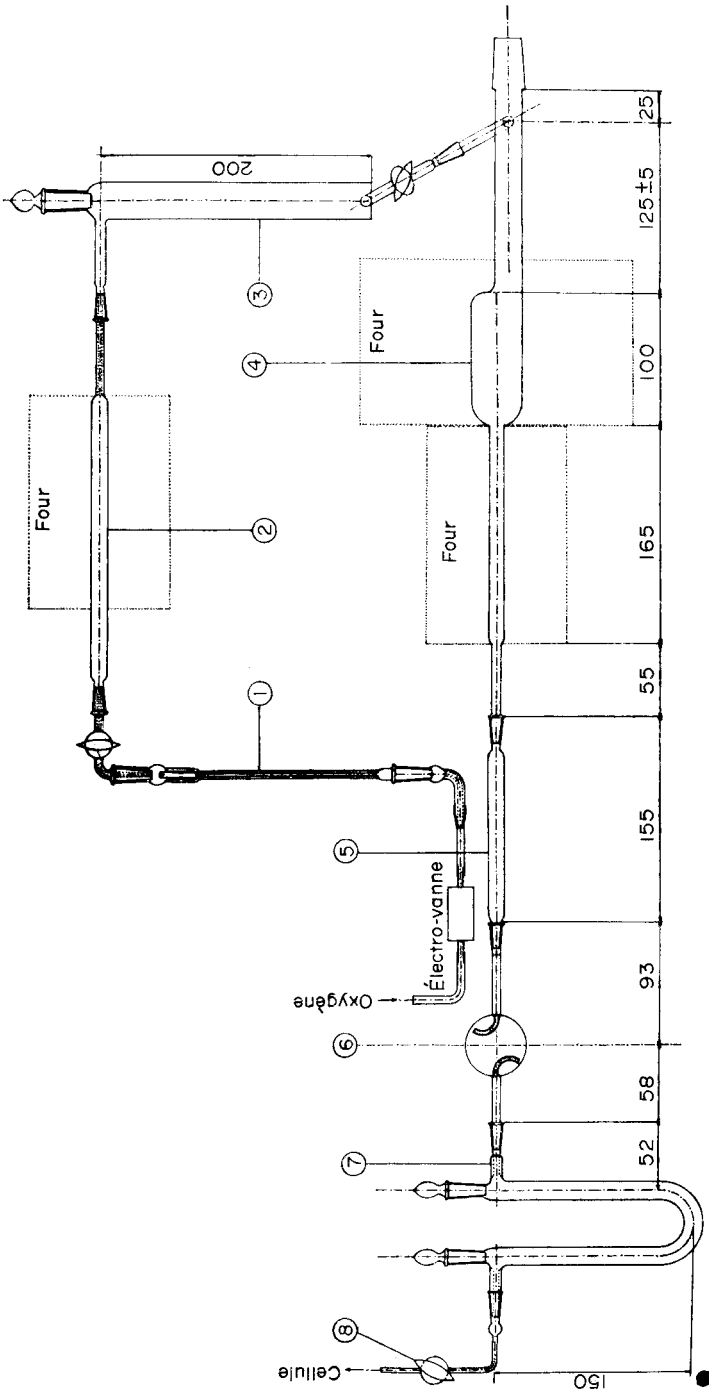


FIG. 1.—Appareil de minéralisation. Légende page 1015.

cellule électrochimique déjà décrite,<sup>4</sup> ne comporte pas, pour notre usage, de circuit gazeux destiné à l'assèchement de l'axe du moteur d'agitation.

Un robinet d'arrêt à 2 voies (8, Fig. 1), sur tube capillaire, est placé juste avant l'entrée des gaz dans le compartiment cathodique, il est relié à la sortie du piège des oxydes de l'azote par un tuyau de polychlorure de vinyle d'environ 0,20 m de longueur et 4 mm de diamètre intérieur.

Le dioxyde de carbone est neutralisé au fur et à mesure de son dégagement dans la solution de perchlorate de baryum dont le pH initial est ajusté à 9. Le dioxyde de carbone est retenu dans la solution jusqu'à un pH d'environ 8,4; en deçà de cette valeur la solution est dite saturée et le gaz s'échappe dans l'atmosphère. Pour éviter la saturation de l'électrolyte, un relais asservi au pH (cf. notice du constructeur) ferme l'électrovanne placée sur le circuit d'oxygène dès que sa valeur atteint 8,8; en aucun cas la valeur du pH ne doit prendre des valeurs inférieures à 8,4 (ce qui correspond à 10 mV sur le millivoltmètre du coulomètre).

### Reactifs

#### *Reactifs pour la minéralisation.*

- Oxygène
- Oxyde de cuivre en fil tamisé (module 29-31, norme NF XII-501) calciné à l'air (*e.g.* Prolabo n° 23 150).
- Amiante sodé (8-20 mesh).
- Perchlorate de magnésium (10-20 mesh).
- Alumine argentée, préparée suivant le mode opératoire décrit par Zimmermann<sup>8</sup> pour la ponce argentée: matières premières—alumine en grain de 1 mm environ; nitrate d'argent pur cristallisé.
- Dioxyde de manganèse.

#### *Réactifs pour coulométrie.*

- Perchlorate de baryum anhydre p.a.
- Carbonate de baryum pur p.a.
- Chlorure de sodium pur p.a.
- Alcool éthylique pur p.a.
- Anhydride tungstique pur.
- Anhydride vanadique pur.

### Mode opératoire

*Mise en condition de l'appareil.* Afin de réduire au minimum le temps de mise en condition de l'appareil le dispositif de minéralisation et la cellule d'électrolyse, sont balayés en permanence, par le courant d'oxygène, même pendant les arrêts de fonctionnement les plus longs; simultanément l'agitation de la cellule est maintenue.

FIG. 1.—Appareil de minéralisation.

1: Rotamètre; 2: Tube en silice transparente, qualité étirée (diamètres: 11/8 mm, longueur 240 mm) pourvu d'un joint conique rodé femelle RIN 00 et prolongé par un tube abducteur (diamètres: 7/2 mm longueur 80 mm) terminé par un joint conique rodé mâle RIN 00; longueur de la garniture d'oxyde de cuivre: 160 mm; ce tube est raccordé au rotamètre par un robinet à 2 voies comportant deux joints coniques rodés mâles RIN 0 et RIN 00; 3: Tube en verre "Pyrex" (diamètres 28/24, longueur 210 mm) pourvu d'un joint conique rodé femelle RIN 00 et d'un tube abducteur comportant un robinet à 2 voies et un joint conique rodé femelle RIN 0. Un joint conique rodé femelle RIN 1 fermé par un bouchon conique rodé femelle RIN 1 fermé par un bouchon conique rodé mâle RIN 1, permet d'y introduire la garniture d'amiante sodé (longueur 100 mm) et de perchlorate de magnésium (longueur 100 mm); 4: Tube à combustion en silice transparente, qualité étirée; 5: Tube en verre "Pyrex" (diamètres 11/8 mm, longueur 150 mm) comprenant deux joints coniques rodés mâle et femelle RIN 00. Longueur de la garniture de perchlorate de magnésium 120 mm; 6: Boule de dilution en verre "Pyrex" (diamètres: 46/42 mm) pourvue de deux joints coniques rodés mâle et femelle RIN 00; 7: Tube en U en verre "Pyrex" (diamètres: 11/8, longueur: 300 mm) pourvu de deux joints coniques rodés mâle et femelle RIN 00 en position latérale. La garniture dioxyde de manganèse (longueur: 180 mm) et perchlorate de magnésium (longueur: 60 mm) est introduite par deux joints coniques rodés femelles fermés par deux bouchons rodés RIN 0; 8: Robinet à deux voies pourvu d'un joint conique rodé RIN 00.

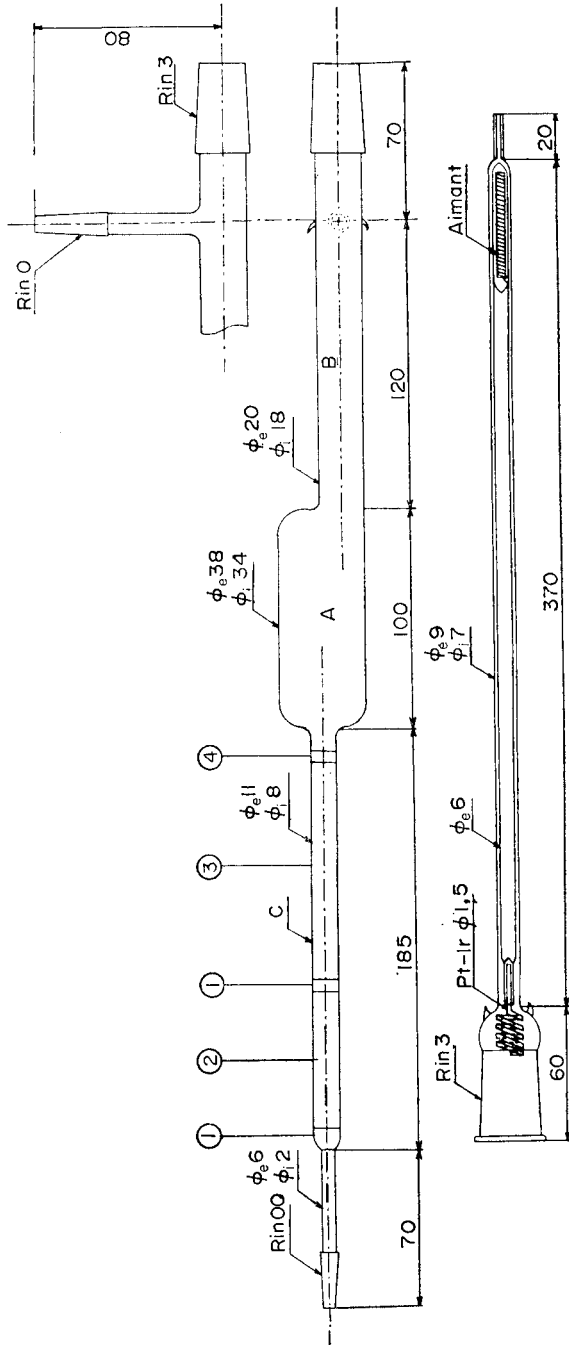


FIG. 2.—Tube à combustion.  
 1: Laine d'argent; 2: Alumine argentée; 3: Oxyde de cuivre en fil; 4: Laine de silice.

Dans ces conditions il suffit de mettre le coulomètre sous tension, de permettre à la solution de se neutraliser, ce qui dure quelques minutes, et de régler le pH à une valeur voisine de 9 (cf. notice du constructeur: test du bouton rouge).

*Détermination du coefficient d'étalonnage.* Le coulomètre est normalement étalonné pour le dosage du carbone dans les aciers: chaque impulsion ou pas de compteur correspond à  $0,5 \mu\text{g}$  de carbone, mais ce coefficient est inutilisable, dans le cadre de notre travail, compte tenu de la précision requise (cf. cid-essous). *Essai à blanc.* En conséquence il est nécessaire de déterminer avant chaque série d'analyses le coefficient d'étalonnage de l'ensemble de l'appareil dans les conditions opératoires. A cette fin, il faut procéder à l'analyse de plusieurs substances-types de teneurs en carbone connues et différentes telles que: Vanilline:  $C\% = 63,15$ ; Acide benzoïque:  $C\% = 68,85$ ; Atropine:  $C\% = 70,55$ ; Diphenylamine:  $C\% = 85,17$ ; Anthracène:  $C\% = 94,34$ ; Pyrène:  $C\% = 95,01$ . En général trois de ces substances-types sont suffisantes pour établir le coefficient d'étalonnage. Chaque substance-type donne une valeur de ce coefficient  $k$  qui se calcule d'après la formule:

$$k = \frac{10 mC}{n} \mu\text{g/pas de compteur}$$

Les paramètres de cette formule ont les significations suivantes:

- $m$  = masse du prélèvement analytique en mg,
- $C$  = teneur centésimale en carbone,
- $n$  = nombre d'impulsions affichées par le compteur.

La moyenne des valeurs de  $k$  trouvées est adoptée comme coefficient d'étalonnage. L'écart entre les valeurs extrêmes ne doit pas être supérieur à  $0,002 \mu\text{g}$  de carbone par pas de compteur.

*Analyse proprement dite.* Fermer le robinet (8, Fig. 1); lorsque la pression d'oxygène dans l'appareil est équilibrée, le rotamètre n'indiquant aucun débit, ouvrir le tube à combustion et introduire la nacelle contenant le prélèvement analytique pesé dans l'hélice de platine du poussoir (cf. Ingram<sup>6</sup>); refermer le tube et attendre à nouveau que la pression soit équilibrée (quelques secondes).

Rétablir le courant gazeux en ouvrant le robinet (8, Fig. 1), laisser balayer 30 sec environ et introduire le poussoir dans la chambre de combustion. Après 5 mn retirer le poussoir; celui-ci est refroidi, *in situ*, de l'extérieur du tube par soufflage d'air comprimé.

Au temps  $t$  déterminé (cf. *Durée d'une analyse*, ci-dessous) relever le nombre de pas de compteur. Le pesage du prélèvement analytique a été effectué pendant le temps de l'analyse précédente.

## DISCUSSION

### *Essai à blanc*

L'appareil étant balayé par le courant d'oxygène, de petites variations de pH se produisent et provoquent une électrolyse et un comptage d'impulsions dont le nombre est l'erreur d'essai à blanc; cette dernière a plusieurs causes.

En premier lieu, la cellule d'électrolyse n'étant pas maintenue à température constante dans un thermostat, elle est, de ce fait, très sensible aux variations de la température ambiante et aux courants d'air.

D'autre part, les interruptions momentanées du courant d'oxygène qui barbote dans l'électrolyte du compartiment cathodique donne lieu à des échauffements et à des refroidissements de la solution.

Toutes les variations de température de l'électrolyte et, par conséquent, du système de détection du point final de titrage (électrode de verre) sont à l'origine des petites variations de pH citées.

En dernier lieu le vieillissement de la silice du tube à combustion et de sa garniture peuvent également être à l'origine d'une partie de la correction d'essai à blanc. Lorsque l'appareil est en état de fonctionnement cette correction d'essai à blanc se chiffre à environ 1-2 pas par minute, valeur non négligeable à l'échelle microanalytique. Cette correction n'est pas effectuée, cependant, comme il apparaît dans le paragraphe ci-après.

*Durée d'une analyse*

La durée d'une analyse est fonction de la quantité de dioxyde de carbone à doser, c'est à dire de la masse du prélèvement analytique pesée et de la teneur C%. Du fait de l'existence d'un essai à blanc il n'est pas possible de préciser à quel moment l'analyse est réellement terminée. Un moyen serait de fixer un temps limite assez grand pour toute analyse et de soustraire au nombre d'impulsions la valeur de la correction d'essai à blanc déterminée dans le même temps. Ce mode opératoire présente deux inconvénients: le premier est l'obligation, pour l'opérateur, de procéder avant toute série d'analyses, à une ou plusieurs déterminations de cet essai à blanc, le deuxième est la prolongation de la durée de chaque analyse.

Pour pallier ces inconvénients nous avons déterminé plusieurs temps d'analyses correspondant chacun, dans nos conditions opératoires, à la neutralisation de quantités de dioxyde de carbone déterminées.

L'examen du déroulement d'une analyse complète, montre qu'il est en effet possible de distinguer deux périodes repérables d'après les déviations du millivolt-mètre-pH mètre. Dans une première période la quasi totalité du dioxyde de carbone arrive dans la cellule et provoque des variations importantes et rapides du pH limitées par la fermeture de l'électrovanne qui interrompt l'arrivée du courant gazeux. Après sa neutralisation il ne se produit plus que des variations petites et lentes du pH correspondant au balayage des trainées de dioxyde de carbone, et à l'essai à blanc.

En conséquence l'opérateur ne connaît pas *à priori* la durée de son analyse mais il est en mesure de voir à quel temps elle est terminée, c'est celui de la fin de la première période. La durée de la première période est variable en fonction de la masse du prélèvement analytique et de sa teneur en carbone; c'est ainsi que pour 2500  $\mu\text{g}$  de carbone elle est de 6 mn environ. Les temps déterminés pour notre appareil sont reportés dans le tableau ci-après.

| Nombre d'impulsions $N$<br>affichées par le compteur | Durée de l'analyse,<br>$mn^*$ |
|--|-------------------------------|
| $N \leq 2000$  | 8                             |
| $2000 < N \leq 2800$                                 | 10                            |
| $2800 < N \leq 3400$                                 | 12                            |
| $3400 < N \leq 4300$                                 | 15                            |
| $4300 < N \leq 5000$                                 | 17                            |

La durée d'une analyse est généralement comprise entre 8 et 12 mn.

*Pesage et masse du prélèvement analytique*

Le pesage est effectué pendant le temps de l'analyse précédente sur balance micro-analytique Mettler M5. Les composés organiques solides et liquides stables, à faible tension de vapeur, sont pesés en nacelle de platine; toutefois lorsque l'addition d'un oxydant, tel que l'hémipentoxyde de vanadium, est nécessaire les nacelles de platine pouvant être rapidement souillées, elles sont remplacées par des nacelles de porcelaine. Les liquides, volatils et hygroscopiques sont prélevés en ampoules de verre "Pyrex" dont le corps, de 2 mm de diamètre et 10 mm de longueur, est prolongé par deux capillaires d'environ 10 mm de longueur. L'un d'eux, laissé ouvert pour permettre le

\* Le temps zéro coïncide avec l'introduction de la nacelle dans la chambre de combustion.

remplissage de l'ampoule par une technique appropriée (à chaud, à froid, sous vide) est ensuite scellé pour le pesage. La masse du prélèvement analytique est généralement comprise entre 1 et 2,5 mg. Lorsque la teneur en carbone du composé analysé est inférieure à 30% la masse peut être supérieure à 3 mg (cf. tableau 1).

### Combustion des composés liquides

Dans le cas des liquides stables, l'un des capillaires de l'ampoule, qui contient le prélèvement analytique pesé, est brisé et placé avec cette dernière dans une nacelle de platine (longueur 26 mm, largeur 6 mm et hauteur 4 mm) qui est ensuite recouverte d'un petit morceau de toile de platine (625 mailles.  $\text{cm}^{-2}$ ).

Dans le cas des composés volatils, l'ampoule dont les deux capillaires restent scellés est placée dans une nacelle de platine plus longue (longueur 40 mm) et recouverte comme précédemment par une toile de platine. L'ampoule éclate lors de son introduction dans la chambre de combustion. Cette technique\* a été éprouvée avec succès depuis plusieurs années dans notre service lors des dosages du carbone et de l'hydrogène par la méthode d'Ingram.<sup>6</sup>

TABLEAU I.—RÉSULTATS OBTENUS SUR QUELQUES SUBSTANCES-TYPES SOUMISES À L'ANALYSE

| Composé                            | $m^*$ , mg  | C, %    |                                     |
|------------------------------------|-------------|---------|-------------------------------------|
|                                    |             | Calculé | Trouvé                              |
| Acide oxalique                     | 6,117 4,394 | 19,05   | 19,1 <sub>1</sub> 19,0 <sub>4</sub> |
|                                    | 4,124 2,988 | —       | 19,0 <sub>2</sub> 19,0 <sub>8</sub> |
| <i>o-o'</i> diethyldithio          | 5,064 5,842 | 23,63   | 23,6 <sub>0</sub> 23,6 <sub>8</sub> |
| phosphate d'ammonium               | 5,440 3,623 | —       | 23,5 <sub>8</sub> 23,6 <sub>4</sub> |
| Acide métatrifluorométhylbenzoïque | 3,030 2,507 | 50,54   | 50,5 <sub>7</sub> 50,5 <sub>0</sub> |
| Trifluoroacétanilide               | 2,581 2,828 | 50,89   | 50,7 <sub>9</sub> 50,6 <sub>9</sub> |
| Acide <i>p</i> -fluorobenzoïque    | 2,323 2,522 | 60,00   | 59,9 <sub>9</sub> 59,6 <sub>3</sub> |
|                                    | 2,506 2,610 | —       | 59,9 <sub>7</sub> 60,0 <sub>2</sub> |
| Monochlorobenzène†                 | 2,082       | 64,02   | 64,0 <sub>7</sub>                   |
| Benzoate de méthyle†               | 1,135 2,094 | 70,57   | 70,5 <sub>9</sub> 70,6 <sub>8</sub> |
| Diphénylamine                      | 1,654 2,264 | 85,17   | 85,3 <sub>8</sub> 85,2 <sub>0</sub> |
| Pyrène                             | 1,565 1,835 | 95,01   | 95,1 <sub>1</sub> 94,9 <sub>6</sub> |

\*  $m$  = masse du prélèvement analytique.

† Composés liquides prélevés en ampoule de verre "Pyrex".

### Retention des oxydes acides de l'azote

Les oxydes acides de l'azote sont retenus sur une garniture de dioxyde de manganèse; son efficacité a une durée variable entre les limites de une ou deux journées de travail à plus d'une semaine, suivant les lots, sans cause apparente. Dans la méthode décrite une mauvaise efficacité du dioxyde de manganèse se décèle très rapidement en se traduisant par des erreurs systématiques par excès de dosage du carbone dans les substances-types azotées. D'une façon générale, le changement de la garniture de dioxyde de manganèse doit être effectué systématiquement en fin de chaque semaine de travail.

\* Technique non publiée mise au point par deux techniciens de notre Service, MM. Roche et Semet.



### *Substances contenant des hétéroéléments*

La technique décrite et les réactifs de rétention utilisés permettent le microdosage du carbone dans les substances contenant de l'hydrogène, de l'azote, des halogènes (dont le fluor), du soufre et du phosphore. La présence de métaux ne gêne pas, à condition, dans le cas de certains d'entre eux comme les métaux alcalins et alcalino-terreux, d'ajouter au prélèvement analytique avant la combustion, un réactif tel que le trioxyde de tungstène ou l'hémipentoxyde de vanadium. A la température de 1000° il est à remarquer que le second de ces réactifs est beaucoup plus efficace que le premier.

### *Substances difficiles à brûler ou à tension de vapeur non négligeable*

L'analyse de certains composés polynucléaires peut conduire à des résultats systématiquement erronés par défaut et apparemment reproductibles. Seuls des prélèvements analytiques de masse très différentes font apparaître une mauvaise reproductibilité et par conséquent l'erreur. Comme précédemment l'addition d'hémipentoxyde de vanadium permet l'obtention de résultats exacts et reproductibles.

D'autres composés solides peuvent se vaporiser partiellement sous l'influence du rayonnement thermique et conduire à des résultats déficitaires. En effet le poussoir chargé de la nacelle contenant le prélèvement analytique, déposée dans l'hélice de platine iridié, n'est pas immédiatement introduit dans la chambre de combustion de sorte que pendant le laps de temps d'attente, la proximité du four peut être à l'origine de ces pertes de substance par vaporisation. Dans ce cas il est nécessaire de refroidir la partie B du tube à combustion à l'aide d'un manchon de refroidissement du type antérieurement décrit<sup>1</sup> préalablement refroidi par immersion au sein de neige carbonique conservée dans un vase à isolation thermique, ou encore par un réfrigérant métallique annulaire refroidi par un courant d'eau.

### *Maintenance de l'appareil*

Pour maintenir l'appareil en état de fonctionnement correct il est nécessaire de procéder systématiquement au renouvellement hebdomadaire des garnitures de perchlorate de magnésium et de dioxyde de manganèse, de l'électrolyte du compartiment cathodique de la cellule d'électrolyse ainsi qu'au remplacement mensuel du tube à combustion et de sa garniture.

## RESULTATS

La méthode décrite a été éprouvée avec succès par l'analyse de plusieurs centaines de substances-types et de composés de recherche. Les résultats objet du tableau I, montrent l'ordre de grandeur des prélèvements analytiques, la précision de la méthode et la variété des composés analysés. Dans le tableau II sont rassemblés une série de composés organiques ayant chacun donné lieu à plusieurs dizaines d'analyses effectuées pendant une période couvrant plusieurs mois et sur les résultats desquelles une étude statistique permet de mettre en évidence les variations de l'écart-type.

L'examen de l'ensemble des deux tableaux montre combien la précision obtenue est supérieure à celle des méthodes dites classiques; en effet lors de l'analyse de substances-types et de composés de recherche solides de même comportement il apparaît que l'erreur absolue n'affecte généralement que la deuxième décimale de la

TABLEAU II.—ÉCARTS-TYPES ESTIMÉS

| Composé                            | n  | C, %      |         | s × 10 <sup>2</sup> , |
|------------------------------------|----|-----------|---------|-----------------------|
|                                    |    | $\bar{x}$ | Calculé | %                     |
| Sulfonal                           | 29 | 36,82     | 36,82   | 6,6                   |
| D. Glucose                         | 28 | 39,97     | 40,00   | 9,2                   |
| Acide <i>p</i> -toluène sulfonique | 27 | 44,16     | 44,20   | 7,3                   |
| <i>p</i> -Nitroaniline             | 30 | 52,19     | 52,17   | 6,5                   |
| Acide acetylsalicylique            | 30 | 59,99     | 60,00   | 10,0                  |
| Vanilline                          | 30 | 63,16     | 63,15   | 11,0                  |
| Anhydride phtalique                | 30 | 64,85     | 64,87   | 9,6                   |
| Disulfure de benzyle               | 30 | 68,22     | 68,24   | 9,8                   |
| Acide benzoïque                    | 30 | 68,85     | 68,85   | 7,7                   |
| Atropine                           | 30 | 70,55     | 70,55   | 9,4                   |
| Acétanilide                        | 30 | 71,12     | 71,09   | 9,3                   |
| Diphénylamine                      | 30 | 85,18     | 85,17   | 13,0                  |
| Anthracène                         | 30 | 94,32     | 94,34   | 20,0                  |
| Pyrène                             | 30 | 94,96     | 95,01   | 17,4                  |

$n$  = nombre de déterminations

$x_1$  = résultat d'une détermination

$$\bar{x} = \text{moyenne des résultats} = \frac{\sum x_1}{n}$$

$$s = \text{écart-type estimé: } s = \sqrt{\frac{\sum(x_1 - \bar{x})^2}{n - 1}}$$

teneur centésimale; pour les hautes teneurs en carbone, l'écart-type relatif reste par ailleurs du même ordre de grandeur que pour les faibles teneurs. Du fait de manipulations plus nombreuses et plus délicates les résultats des analyses des composés liquides pesés en ampoule sont toutefois moins reproductibles.

La méthode décrite est simple, rapide et de grande fiabilité; elle est également caractérisée par la grande facilité de sa mise en oeuvre. Le coulomètre est identique à celui qui est utilisé par ailleurs pour le microdosage de l'oxygène;<sup>4</sup> il suffit de lui adapter un appareil permettant le décalage du pH du point final de titrage pour permettre de l'utiliser pour le microdosage du soufre.<sup>9,10</sup> Ainsi le même appareil peut permettre le dosage de trois éléments cités (C, O, S) sous réserve de lui associer dans chaque cas le dispositif de minéralisation approprié.

**Summary**—A rapid simple method is described for the determination of carbon in organic compounds. The technique is based on a flash-combustion of the weighed sample (1–3 mg) in a hot empty combustion chamber at 950–1050° and swept by a stream of oxygen at a rate of 80–100 ml/min. Together with this flash and dynamic combustion in oxygen, a cupric oxide filling at 850° is necessary. Halogens and sulphur oxidation products are retained by means of a silvered alumina filling at 750–800°. Water and acidic oxides of nitrogen are absorbed at room temperature by means of magnesium perchlorate and manganese dioxide respectively. Carbon dioxide is absorbed in the cathodic compartment of an automatic coulometer and generates H<sup>+</sup> ions which are neutralized by OH<sup>-</sup> obtained by electrolysis. This method makes possible the determination of carbon in compounds containing halogens (including fluorine), phosphorus and metals. However, some metal compounds with polynuclear rings in their molecules give low results and require the addition of an oxidant to the sample in the boat for complete combustion. Vanadium pentoxide seems to be the best

oxidant in the present working conditions. Solid samples are weighed and analysed in platinum or porcelain boats; liquid samples are weighed in Pyrex capillaries which are laid in platinum boats and covered with a small piece of platinum gauze. When normal liquid samples are analysed, one tip of the capillary is broken before its introduction into the combustion tube but in the case of volatile liquid samples the sealed capillary is introduced into the combustion chamber, where it explodes. The precision obtained is better than that of the classical methods.

**Zusammenfassung**—Ein schnelles einfaches Verfahren zur Bestimmung von Kohlenstoff in organischen Verbindungen wird beschrieben. Es beruht auf der Schnellverbrennung der gewogenen Probe (1–3 mg) in einer heißen Verbrennungskammer bei 950–1050°, die mit einem Sauerstoffstrom von 80–100 ml/min gespült wird. Zusammen mit dieser schnellen dynamischen Verbrennung in Sauerstoff ist eine Kupferoxidfüllung bei 850° notwendig. Halogene und Schwefeloxida-tionsprodukte werden durch eine Silberfüllung auf Tonerde bei 750–800° zurückgehalten. Wasser und saure Stickstoffoxide werden bei Zimmertemperatur mit Magnesiumperchlorat bzw. Mangandioxid absorbiert. Kohlendioxid wird im Kathodenraum eines automatischen Coulometers absorbiert und erzeugt H<sup>+</sup>-Ionen, die durch elektrolytisch erhaltene OH<sup>-</sup>-Ionen neutralisiert werden. Dieses Verfahren ermöglicht die Bestimmung von Kohlenstoff in Verbindungen, die Halogene (auch Fluor), Phosphor und Metalle enthalten. Einige Metallverbindungen mit mehrkernigen Ringen geben jedoch zu geringe Ergebnisse und erfordern Zugabe eines Oxidationsmittels zur Probe im Schiffchen, um vollständige Verbrennung zu erzielen. Vanadumpentoxid scheint unter den angegebenen Arbeitsbedingungen das beste Oxidationsmittel zu sein. Feste Proben werden in Platin- oder Porzellanschiffchen eingewogen und analysiert. Flüssige Proben werden in Pyrex-Kapillaren eingewogen, die man in Platinschiffchen legt und mit einem kleinen Stück Platinnetz bedeckt. Werden normale flüssige Proben analysiert, so wird vor dem Einführen ins Verbrennungsrohr eine Spitze der Kapillaren abgebrochen; bei flüchtigen flüssigen Proben wird die abgeschmolzene Kapillare ins Verbrennungsrohr eingeführt, wo sie explodiert. Die erzielte Genauigkeit ist besser als die der herkömmlichen Methoden.

#### BIBLIOGRAPHIE

1. R. H. Reitsema et N. L. Allphin, *Anal. Chem.*, 1961, **33**, 355.
2. R. Levy, *Bull. Soc. Chim. France*, 1968, 2173.
3. K. Abresch et I. Claassen, *Coulometric Analysis* (transl. L. L. Leveson). Chapman & Hall, London, 1965.
4. D. Fraisse et R. Levy, *Bull. Soc. Chim. France*, 1968, 445.
5. F. Martin, A. Floret et J. Lemaitre, *ibid.*, 1964, 1836.
6. G. Ingram, *Microchem. J., Symp. Ser.*, Vol. 2, *Microchemical Techniques*, p. 495. Wiley, New York, 1962.
7. B. Cousin, *Bull. Soc. Chim. France*, 1969, 2915.
8. W. Zimmermann, *Mikrochem. Mikrochim. Acta*, 1943, **31**, 149.
9. E. Debal et R. Levy, *Bull. Soc. Chim. France*, 1968, 426.
10. D. Fraisse et R. Levy, *Compt. Rend.*, 1970, **271**, 49.

# PHOTOMETRIC COMPLEX-FORMATION TITRATION OF SUBMICROMOLE AMOUNTS OF METAL—II THE PRESENCE OF OTHER METALS

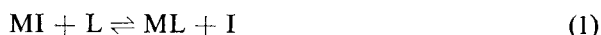
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**Summary**—End-point extrapolation with the aid of a tangent to the spectrophotometric titration curve has been discussed theoretically for the metal-indicator complex MI with a ligand L in the presence of two other metals ( $P_1$  and  $P_2$ ). It was found that a titration end-point can only be determined when the reaction of  $P_1$  and  $P_2$  with L takes place only negligibly during the titration of M. Two cases of practical interest can be distinguished. The metals may react either before or after the titration has been completed. For both situations titration conditions have been derived. With these titration conditions suitable experimental conditions can directly be derived from diagrams which were introduced in a previous paper. The theory developed has been applied to mixtures of manganese and magnesium but is generally applicable.

IN A RECENT paper<sup>1</sup> titration conditions were derived for the titration of submicromole amounts of a metal M in the presence of an approximately equivalent amount of indicator I with a ligand L according to the reaction



Based on these relationships a procedure was presented for selection of suitable titration conditions for the extrapolation of the end-point by drawing a tangent to the titration curve at the point where 1/10 of the metal is still bound to the indicator.

In this paper the presence of two other metals  $P_1$  and  $P_2$  will be taken into account. In the first part the theory is extended and additional titration conditions are derived for prediction of the most suitable experimental conditions for a titration. In the second part the theory is applied to the selection of suitable titration conditions for mixtures of manganese and magnesium. The procedure is quite general; experimental conditions for mixtures of other metals can analogously be deduced from the corresponding diagrams.

## THEORY

It is supposed that only 1:1 complexes are formed between M and I, and that the metals  $P_1$  and  $P_2$  do not react with the indicator. Terminology and symbols used are the same as in the previous paper.<sup>1</sup> Additionally we introduce  $Z_{P_1} = C_{P_1} \cdot K_{P_1L}$  and  $Z_{P_2} = C_{P_2} \cdot K_{P_2L}$ .

The formation of  $P_1L$  and  $P_2L$  is not considered as a side-reaction, but as a competing main reaction, which will separately be introduced in the mathematical formulations. Therefore the side-reaction coefficients  $\alpha_{L(P_1)}$  and  $\alpha_{L(P_2)}$  should not be included in the conditional constant  $K_{M'L}$ .

From the mass balances the titration parameter is

$$f = \frac{C_I}{C_M} = \frac{[ML]}{C_M} + \frac{[L]}{C_M} + \frac{[P_1L]}{C_M} + \frac{[P_2L]}{C_M} \quad (2)$$

By successive substitution, as shown in the previous paper,<sup>1</sup> a full form of the relationship  $f = f(mi)$  can be obtained, but it is rather complicated for the derivation of titration conditions. So we follow a different rule. With the aid of a computer a large number of  $mi$ - $f$  relationships were calculated for various combinations of  $Z_M$ ,  $Z_I$ ,  $C_{P_1}/C_M$ ,  $C_{P_2}/C_M$ ,  $Z_{P_1}$ ,  $Z_{P_2}$  and  $\beta$ . It followed, as could be expected, that a titration end-point can only be determined when during the titration of M the reaction of the metals  $P_1$  and  $P_2$  with L hardly takes place. They may react either before reaction (1) starts or after reaction (1) has been completed. We will discuss the different cases separately.

(A) *M is titrated before  $P_1$  and  $P_2$  are bound to L*

In this case the exact  $mi$ - $f$  relation may be approximated by

$$f = (1 - mi) - \frac{mi}{Z_I(1 - mi/\beta)} + \frac{1}{mi} \cdot \left(\frac{Z_I}{Z_M}\right) \cdot (1 + Z_{P_1} + Z_{P_2}) \quad (3)$$

$$= f_1 + f_2 + f_3.$$

Equation (3) is similar to the equation derived in the previous paper,<sup>1</sup> the terms  $f_1$  and  $f_2$  are identical, but the last term,  $f_3$ , is here multiplied by a constant  $(1 + \sum Z_{P_i})$ .

The term  $f_3$  involves the relative contributions of the free species and the chelates  $P_1L$  and  $P_2L$ ;  $f_3 = 1/C_M([L] + [P_1L] + [P_2L])$ . Substitution from the equilibrium constants gives:

$$f_3 = \frac{[L]}{C_M} (1 + K_{P_1L}[P_1] + K_{P_2L}[P_2]).$$

As the contributions of the chelates  $P_1L$  and  $P_2L$  are assumed to be negligible close to the end-point, the total concentrations of the competing metals can be substituted for the particular equilibrium concentrations and the last term is

$$f_3 = \frac{[L]}{C_M} (1 + Z_{P_1} + Z_{P_2}).$$

As shown in the previous paper,<sup>1</sup> the term  $[L]/C_M$  can be simplified to  $(Z_I/Z_M)/mi$ , which yields the expression in equation (3).

Evidently, the conclusions about the end-point determination, as derived previously,<sup>1</sup> can also be applied here, viz.

$$\log Z_I > 1 \quad (4)$$

and

$$T = \log \frac{Z_M}{Z_I(1 + Z_{P_1} + Z_{P_2})} > 3.5. \quad (5)$$

The factor  $(1 + Z_{P_1} + Z_{P_2})$  can be taken as a side-reaction coefficient,<sup>2</sup>  $\alpha_{L(P_1P_2)}$ , which reflects the competition between  $P_1$ ,  $P_2$  and M for the ligand L. The influence of  $(Z_{P_1} + Z_{P_2})$  is illustrated in Fig. 1. The curves are calculated on the basis of the exact form of the function  $mi = F(f)$ , for a substoichiometric amount of indicator ( $\beta = C_I/C_M = 0.7$ ) and different values of  $(Z_{P_1} + Z_{P_2})$ . Only the curves *a* and *b* are of practical interest. The deviation between the curves *a*, *b* and *c*, and those calculated with the aid of the approximate equation (3) are so small that the curves coincide.

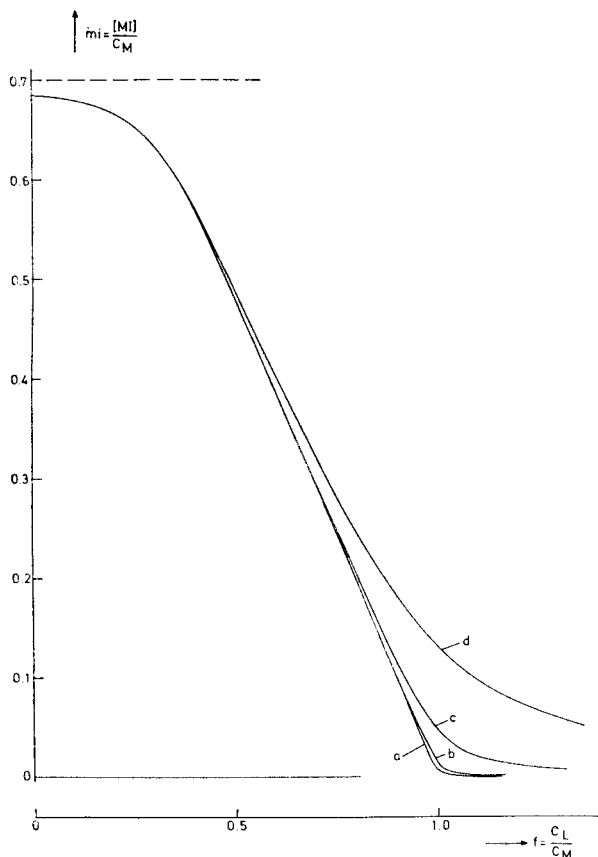


FIG. 1.—Theoretical titration curves representing the influence of  $P_1$  and  $P_2$  for different values of  $(Z_{P_1} + Z_{P_2})$ . The curves are constructed with  $Z_M = 4 \times 10^6$ ,  $Z_I = 100$ ,  $\beta = 0.7$  (a substoichiometric amount of indicator) and  $\Sigma Z_P = 1$  (curve *a*,  $T = 4.3$ ),  $\Sigma Z_P = 10$  (curve *b*,  $T = 3.6$ ),  $\Sigma Z_P = 100$  (curve *c*,  $T = 2.6$ ) and  $\Sigma Z_P = 1000$  (curve *d*,  $T = 1.6$ ).

(B)  $P_1$  and  $P_2$  are bound to  $L$  respectively before and after the titration of  $M$

For a direct determination of  $M$  from the successive complexation of  $P_1$ ,  $M$  and  $P_2$ , two break-points are required in the titration curve. It will be shown that the influence of  $P_2$  is restricted to the second end-point. Figures 2 and 3 show the influence of metal  $P_1$  on the titration curve for different values of  $Z_{P_1}$ . The curves are calculated by means of an exact equation. For convenience  $Z_{P_2}$  has been taken as unity in these figures. It is obvious that a first break-point can only be determined from curve *g*, where  $Z_{P_1} = 10^{12}$ . However, in this case extreme conditions have to be satisfied, i.e.  $Z_I \gg 1$ ,  $\beta = 2$  and  $K_{P_1L} \gg K_{ML}$ , which can never be realized in practice. This implies that a direct determination of  $M$  is impossible.

From the second end-point the sum of  $M$  and  $P_1$  can be determined; another determination of  $P_1$  is necessary for a calculation of the amount of  $M$ .

In the following, the discussion is restricted to the determination of the second end-point. It will be shown that the presence of  $P_2$  leads to titration conditions

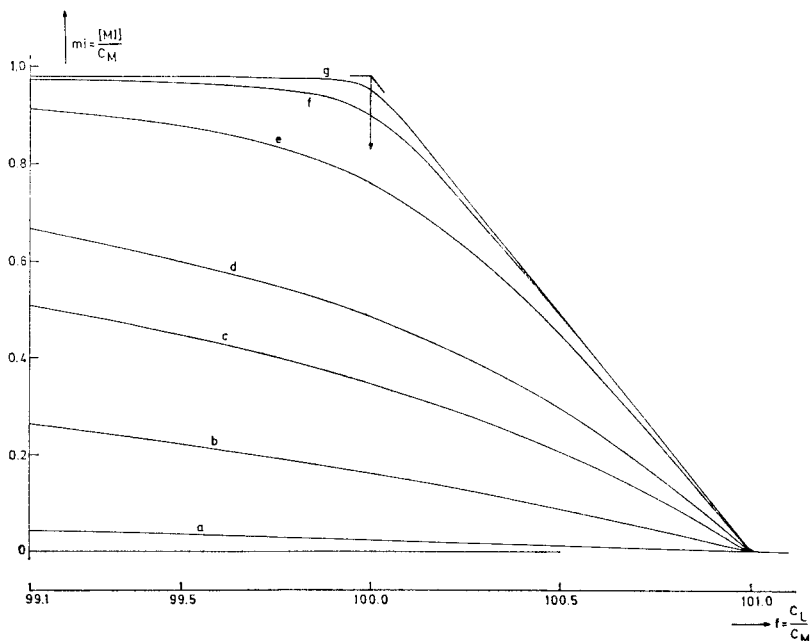


FIG. 2.—Theoretical titration curves representing the influence of  $P_1$  for different values of  $Z_{P_1}$ . The curves are constructed with  $Z_M/Z_I = 4 \times 10^3$  and  $Z_{P_2} = 1$ , making  $T = 4.3$ . Excess of indicator is present ( $\beta = 2$ ),  $P_1$  is present in a 100-fold excess ( $C_{P_1}/C_M = 100$ ). The values of  $Z_{P_1}$  are  $10^7$  (curve *a*,  $S = -1.6$ ),  $10^8$  (curve *b*,  $S = -0.6$ ),  $4 \times 10^8$  (curve *c*,  $S = 0$ ),  $10^9$  (curve *d*,  $S = 0.4$ ),  $10^{10}$  (curve *e*,  $S = 1.4$ ),  $10^{11}$  (curve *f*,  $S = 2.4$ ) and  $10^{12}$  (curve *g*,  $S = 3.4$ ).

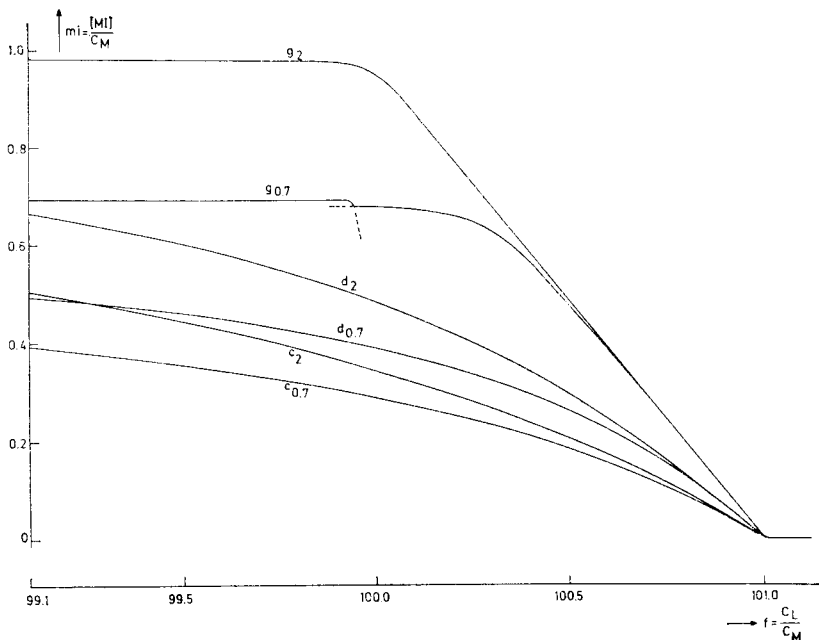


FIG. 3.—The curves  $c_2$ ,  $d_2$  and  $g_2$  are the same as in Fig. 2 ( $\beta = 2$ ). The other curves are constructed with  $\beta = 0.7$  in order to show the influence of a deficit of indicator.

analogous to the previous case and that the presence of  $P_1$  leads to a further titration condition.

On substitution from the particular mass balances and stability constants the term  $[P_1L]/C_M$  in equation (2) can be written as

$$\frac{[P_1L]}{C_M} = \left(\frac{C_{P_1}}{C_M}\right) \cdot \frac{1}{1 + \left(\frac{C_{P_1}}{C_M} \cdot \frac{1}{Z_{P_1}} \cdot \frac{C_M}{[L]}\right)}. \quad (6)$$

When  $\left(\frac{C_{P_1}}{C_M} \cdot \frac{1}{Z_{P_1}} \cdot \frac{C_M}{[L]}\right) < 0.1$ , which appears to be satisfied in all practical cases, equation (6) may be approximated by

$$\frac{[P_1L]}{C_M} = \left(\frac{C_{P_1}}{C_M}\right) \left\{1 - \left(\frac{C_{P_1}}{C_M} \cdot \frac{1}{Z_{P_1}} \cdot \frac{C_M}{[L]}\right) + \left(\frac{C_{P_1}}{C_M} \cdot \frac{1}{Z_{P_1}} \cdot \frac{C_M}{[L]}\right)^2\right\}. \quad (7)$$

Substitution of the function  $[L] = f(mi)$  yields the final form of this term. Hence the equation for  $f$  is

$$\begin{aligned} f &= \left(\frac{C_{P_1}}{C_M}\right) + (1 - mi) - \frac{mi}{Z_1(1 - mi/\beta)} + \frac{1}{mi} \cdot \left(\frac{Z_1(1 + Z_{P_2})}{Z_M}\right) \\ &\quad - \left(\frac{C_{P_1}}{C_M}\right)^2 \cdot \left(\frac{Z_M}{Z_1 \cdot Z_{P_1}}\right) \cdot \left\{\frac{mi}{(1 - mi)(1 - mi/\beta)}\right\} \\ &= f_0 + f_1 + f_2 + f_3 + f_4. \end{aligned} \quad (8)$$

The meaning of  $f_0$  will be obvious. The terms  $f_1$ ,  $f_2$  and  $f_3$  have been discussed in the previous section. The term  $f_4$  reflects the influence of the incomplete formation of  $P_1L$  near the second break-point (see Figs. 2 and 3).

#### *The end-point determination and the titration conditions*

For the determination of the end-point and the choice of the titration conditions the same line is followed as in the previous paper.

The end-point is found from the intersection of the tangent at  $mi_0 = 0.1$  with the  $f$ -axis. A statistical error of about 0.4% for drawing the tangent is assumed. In order to maintain the total error smaller than 1%, the systematic deviation  $\Delta f$  has to be smaller than 0.6%.

$\Delta f_e = f_e - \left(\frac{C_{P_1}}{C_M} + 1\right)$  can be calculated from equation (8) by means of the relationship

$$f_e = f(mi_0) - mi_0 \cdot \left(\frac{df}{dmi}\right)_{mi_0}. \quad (9)$$

As the terms  $f_1$ ,  $f_2$  and  $f_3$  are similar to those in the previous paper,<sup>1</sup> the same approach can be used, and their contribution to  $\Delta f_e$  (for  $mi_0 = 0.1$ ) expressed approximately [cf. equation (17), Ref. 1] as

$$\Delta f_{0.1.2.3} = \left(\frac{2}{mi_0}\right) \cdot \left(\frac{Z_1(1 + Z_{P_2})}{Z_M}\right). \quad (10)$$



The contribution of the last term in (8) to  $\Delta f_e$  is

$$\Delta f_4 = \left\{ \frac{Z_M/Z_I}{Z_{P_1}/\left(\frac{C_{P_1}}{C_M}\right)^2} \right\} \cdot \left\{ \frac{mi_0}{(1-mi_0)(1-mi_0/\beta)} \right\} \cdot \left( 1 + \frac{1}{\beta} \right). \quad (11)$$

Taking  $\Delta f_e$  as smaller than 0.3% and substituting  $\beta = 1$  and  $mi_0 = 0.1$ , equations (10) and (11) lead to the titration condition

$$T = \log \frac{Z_M}{Z_I(1 + Z_{P_2})} > 3.8 \quad (12)$$

and an additional condition

$$S = \log \left\{ \frac{Z_{P_1}}{\left(\frac{C_{P_1}}{C_M}\right)^2} \right\} - \log \frac{Z_M}{Z_I} = \log \left( \frac{K_{P_1L}}{C_{P_1}} \right) - \log \left( \frac{\text{Ind}K_{ML}}{C_M} \right) > 1 \quad (13)$$

where  $\text{Ind}K_{ML}$  is  $K_{M'L'(ML)}/Z_I$ .

As in practice absorbance-titrant volume curves are measured, sufficient formation of MI must occur. For this reason a minimum of  $Z_I$  is adopted, just as in the previous paper:

$$\log Z_I > 1. \quad (14)$$

It can be noted that we checked equations (10) and (11) by calculating the systematic deviations from the original set of exact equations. In all cases of practical interest ( $\Delta f_e < 0.6\%$ ) the agreement between both series of calculations was found to be better than 0.1%.

### (C) $P_1$ and $P_2$ are bound to L before the titration of M

From a comparison of the results of the two previous sections it can easily be seen that  $Z_{P_2}$  will disappear from the  $T$ -condition and that an additional  $S$ -condition appears for  $P_2$ , resulting in the following conditions

$$T = \log \left( \frac{Z_M}{Z_I} \right) > 3.8 \quad (15)$$

$$S_{P_1} = \log \left\{ \frac{Z_{P_1}}{\left(\frac{C_{P_1}}{C_M}\right)^2} \right\} - \log \left( \frac{Z_M}{Z_I} \right) = \log \left( \frac{K_{P_1L}}{C_{P_1}} \right) - \log \left( \frac{\text{Ind}K_{ML}}{C_M} \right) > 1 \quad (16)$$

$$S_{P_2} = \log \left\{ \frac{Z_{P_2}}{\left(\frac{C_{P_2}}{C_M}\right)^2} \right\} - \log \left( \frac{Z_M}{Z_I} \right) = \log \left( \frac{K_{P_2L}}{C_{P_2}} \right) - \log \left( \frac{\text{Ind}K_{ML}}{C_M} \right) > 1 \quad (17)$$

$$\log Z_I > 1. \quad (18)$$

#### Remark

At the beginning of the theoretical section it was supposed that the metals P do not react with I. For the metal P, which reacts with L after the titration of M, this is a necessary condition, as the absorption of PI will generally interfere in the end-point determination.

When P is bound to L before M, PI will hardly be present near the end-point for M. This means that the reaction  $P + I \rightleftharpoons PI$  does not interfere in the end-point determination. The titration conditions remain valid. As the PI formation may be regarded as a side-reaction of the formation of PL, the corresponding side-reaction coefficient has to be introduced into the conditional constant  $K_{PL}$  and so in the  $S$ -condition, which in this case becomes

$$S = \log \left( \frac{\text{Ind}K_{PL}}{C_P} \right) - \log \left( \frac{\text{Ind}K_{ML}}{C_M} \right) > 1. \quad (19)$$

### Discussion

Equations (3) and (8) are approximate relationships. In some cases the approximate curves may appreciably deviate from the exact curves, as for instance in case (B) when the  $S$ -condition is only just satisfied and when  $mi > 0.9$ . However, this is rather unimportant as the deviations can always be neglected in the region  $mi < 0.1$ , in which the end-point is determined and from which the titration conditions are derived. There, the approximations are justified. The titration conditions can then be considered exact. The theory can be applied to problems already solved. For instance, Kotrlý *et al.*<sup>3</sup>, found a suitable procedure for the analysis of low concentration Bi–Pb mixtures and indicated how the shape of the experimental curves can be understood. It can be shown that the titration conditions above are satisfied in this case. Of more importance, however, is the reverse procedure, namely the derivation of suitable experimental conditions from the conditional constants, side-reaction coefficients *etc.*

In the following section it will be shown how from the titration conditions in combination with the diagrams discussed in the previous paper<sup>1</sup> the optimum experimental conditions can be derived for a particular case. The procedure can analogously be applied to other mixtures and has found wide applicability in the author's laboratory for the analysis of two- and three-component samples. A number of cases will be published separately. In this paper the illustration will be restricted to mixtures of manganese and magnesium.

In some cases better results were obtained by using back-titrations. The titration conditions for this type of titration differ slightly from those for the direct titrations; they will be discussed in a later paper.

### EXPERIMENTAL

It has been shown<sup>1</sup> that a convenient way to select experimental conditions is by means of a diagram in which  $\log K_{ML'(ML)'}'$ ,  $\log \alpha_{M(X)}$  (the partial side-reaction coefficient of  $M$  with  $X$ ) and  $\log \chi_1 (= C_I \cdot K_{M1'(M1)'}')$  are plotted *vs.* the pH. Figures 4 and 5 show diagrams for Mg and Mn, based upon data given by Ringbom.<sup>2</sup>

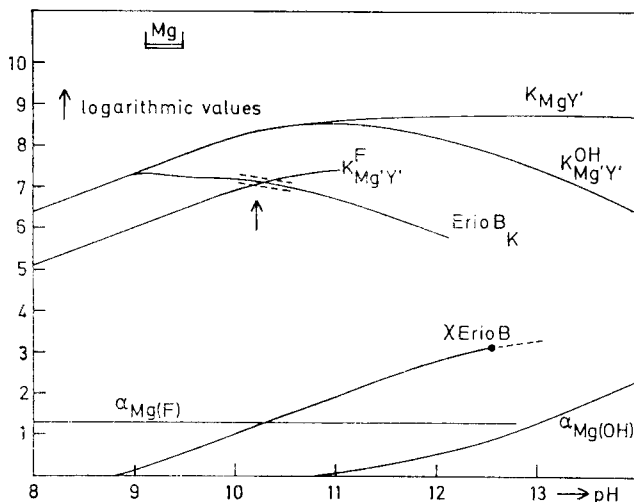


FIG. 4.—The influence of the medium on the  $K$ -,  $\chi$ - and  $\alpha$ -values of magnesium. The curves are constructed for  $C_I = 10^{-4}M$  and  $C_F = 1M$ .

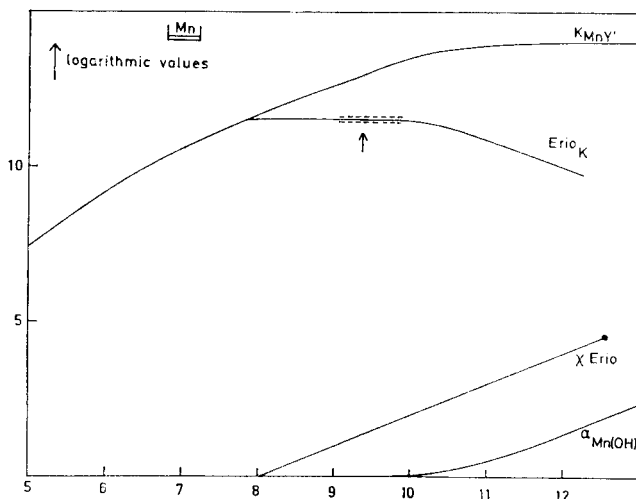


FIG. 5.—The influence of the medium on the  $K$ -,  $\chi$ - and  $\alpha$ -values of manganese. The  $\chi$ -curve is constructed with  $C_I = 10^{-4}M$ .

First we will discuss the separate titration of magnesium and manganese and afterwards the titration of their mixture.

#### Magnesium

There are many indicators known for Mg, of which Eriochrome Blue Black B (Erio B) is the most suitable for microtitrations. The reason is that in the pH ranges in which  $\log Z_I = \log \chi_I - \log \alpha_{M(X)} > 1$  holds for the different indicators, Erio B gives the highest value for  $Z_M/Z_I$  ( $C_I \approx 10_M^{-4}$ ;  $\lambda_{MI} = 530$  nm). Because of a colour transition of the free indicator the  $\alpha_{Erio B}$ -line ends at pH = 12.5.

The most suitable pH range is 10–10.5. From  $Erio B K = 7.2$  it follows that the minimum concentration of Mg is  $pC_{Mg} = 3.7$ . This was confirmed experimentally.

#### Manganese

The most suitable indicator is Erio B ( $\lambda = 530$  nm;  $\Delta\epsilon = 1800$  l. mole $^{-1}$ . mm $^{-1}$ ). The pH-range (see Fig. 5) in which  $\log Z_I > 1$  and  $Z_M/Z_I$  has its maximum, is 9–10. The second titration condition  $\log (Z_M/Z_I) > 3.5$  is satisfied for  $C_M > 10_M^{-9}$ . It will be obvious that the limit of determination is determined by the molar absorptivity and so by the instrumental equipment.

#### Manganese in the presence of magnesium

This case is related to case (A). The following titration conditions have to be satisfied:

1. Erio B should not react with Mg.

$$2. \log Z_{Erio B} = \log \chi_{Erio B} - \log \alpha_{Mn(OH)} > 1 \text{ and} \quad (20)$$

$$3. T = \log \frac{Z_{Mn}}{Z_{Erio B}(1 + Z_{Mg})} = \log \frac{C_{Mn} \cdot Erio B K}{(1 + C_{Mg} \cdot K_{Mg'Y'})} > 3.5. \quad (21)$$

The first condition is satisfied for pH < 9 and the second for pH > 9. Consequently only pH = 9 satisfies both.

The titration can be improved by adding fluoride, which reacts with Mg. For  $C_F = 1M$  the first condition is satisfied for pH < 10.3 (Fig. 4). The second condition again gives pH > 9.0. From the third condition it follows that a larger excess of Mg can be tolerated. It has experimentally been verified that a 30-fold excess of Mg does not interfere in a micromole titration of manganese ( $C_{Mn} = 10^{-4}M$ ;  $T = 3.7$ ).

*The sum of manganese and magnesium*

According to cases (B) and (C) the following titration conditions have to be satisfied:

$$\log Z_{\text{Er}10\text{B}} > 1. \quad (22)$$

$$\log \left( \frac{Z_{\text{Mg}}}{Z_{\text{Er}10\text{B}}} \right) > 3.8. \quad (23)$$

$$S = \log \left( \frac{\text{Er}10\text{B} K_{\text{Mn}}}{C_{\text{Mn}}} \right) - \log \left( \frac{\text{Er}10\text{B} K_{\text{Mg}}}{C_{\text{Mg}}} \right) > 1. \quad (24)$$

The first and second conditions are similar to those for the single titration of Mg. It follows that  $\text{pH} = 10.0\text{--}10.5$  and  $C_{\text{Mg}} > 10^{-3.3}M$ . The last condition [which comes from equation (19)] gives for  $\text{p}C_{\text{Mg}} = 3.3$ ,  $S = \text{p}C_{\text{Mn}} + 0.9 > 1$ , which condition is satisfied in all practical cases.

The method has been applied to the analysis of Mn–Mg alloys and to samples of mixtures of  $\text{K}_2\text{MnF}_4$  and mixtures of  $\text{KMnF}_3\text{--KMgF}_3$  in which the ratio Mg/Mn varied from 0.1 to 0.3. The results agreed within 2% with the measurements of magnetic susceptibility, heat conductivity and spin relaxation performed by solid-state physicists.

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**Zusammenfassung**—Die Endpunktsbestimmung durch Extrapolation mit Hilfe einer Tangente an die spektrophotometrische Titrationskurve wird am Metall-Indikator-Komplex MI mit einem Liganden L in Gegenwart zweier anderer Metalle ( $P_1$  und  $P_2$ ) theoretisch diskutiert. Ein Titrationsendpunkt kann nur gefunden werden, wenn während der Titration von M die Reaktion von  $P_1$  und  $P_2$  mit L zu vernachlässigen ist. Man kann zwei Fälle von praktischer Bedeutung unterscheiden: die Metalle können vor oder nach Ende der Titration reagieren. Für beide Fälle wurden die Titrationsbedingungen abgeleitet. Aus diesen Bedingungen kann man an Hand früher eingeführter Diagramme direkt die geeigneten Versuchsbedingungen ableiten. Die Theorie wurde auf Gemische von Mangan und Magnesium angewandt; sie ist jedoch allgemein verwendbar.

**Résumé**—On discute théoriquement de l'extrapolation du point de fin de dosage à l'aide d'une tangente à la courbe spectrophotométrique de titrage pour le complexe métallo-indicateur MI avec un coordinaat L en la présence de deux autres métaux ( $P_1$  et  $P_2$ ). On a trouvé qu'un point de fin de titrage ne peut être déterminé que quand la réaction de  $P_1$  et  $P_2$  avec L n'a lieu que de manière négligeable durant le titrage de M. On peut distinguer deux cas d'intérêt pratique. Les métaux peuvent réagir soit avant, soit après que le titrage ait été achevé. Pour les deux situations, des conditions de titrage ont été déduites. Avec ces conditions de titrage, on peut déduire directement des conditions expérimentales convenables à partir de diagrammes qui ont été présentés dans un mémoire antérieur. On a appliqué la théorie développée à des mélanges de manganèse et de magnésium, mais elle est généralement applicable.

## REFERENCES

1. J. Kragten, *Talanta*, 1971, **18**, 311.
2. A. Ringbom, *Complexation in Analytical Chemistry*, p. 38. Interscience, New York, 1963.
3. S. Kotrlý and J. Vřešál, *Collection Czech. Chem. Commun.*, 1960, **25**, 1148.

## STATISTICAL CHOICE OF STANDARD SAMPLES AND PRECISION OF ANALYSIS IN EMISSION SPECTROSCOPY

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**Summary**—An approach utilizing mathematical statistics to aid the choice of standard concentrations in emission spectroscopy is presented. The method is applied to the analysis of isoformed samples by the tape method. Some other possible applications (*eg.* X-ray, fluorescence, absorption photometry) are briefly discussed.

EVALUATING spectrographic or photometric data implies using a calibration function based on a series of data, which have been obtained by measuring the intensity of emission or absorption of standards of known composition. The standards are usually chosen so that their contents of the component to be determined are about equally spaced over the concentration range of interest. The method of least squares is often used to compute the calibration function.

This approach, empirical though it is, is justified when (*a*) the mathematical form of the calibration function is not known, (*b*) the choice of standards is very restricted, (*c*) the number of analyses is small.

Quite often, however, a different, more theoretical approach seems to offer a means whereby the information, that lies concealed within the experimental data, may be better utilized. This approach can be used when (*a*) the true mathematical form of the calibration function is known, save for the values of a few parameters, the values of which can be estimated by analysing known standards, (*b*) there is a comprehensive range of standards to choose from (this particularly extends the applicability of the concept to all spectrographic analysis work employing some sort of "isoformation" of the sample since blanks are available and it is possible to use synthetic standards), (*c*) the number of analyses is large. By "isoformation" we mean any method used for controlling matrix effects in optical spectrometry.<sup>1</sup>

If these conditions are fulfilled, it should be of interest to study the choice of standards, considering speed, accuracy and economy of analysis. A convenient tool for doing this is provided by mathematical statistics.

The aim of the present work has therefore been, on the one hand, to study the possibilities of improving the precision of analysis by using mathematical statistics to aid in the choice of standards and the estimation of the parameters, assuming that the mathematical form of the calibration function is known, and on the other hand, to consider situations where the accuracy is considered less important than the speed and economy of analysis. The possibilities of using the information obtained by the

statistical technique for economic optimization have also been considered worthy of investigation.

Primarily, the work has been conducted in order to facilitate the large scale emission spectrographic analysis work at Sveriges geologiska undersökning<sup>1</sup> (the Geological Survey of Sweden) but similar arguments can naturally be used whenever a reliable mathematical model can be estimated.

#### THEORY

##### *A mathematical model for intensity measurements (including design of the calibration function)*

It should always be kept in mind that the statistical results will hold only if the model is correct and, in order to ensure this, the conditions required for the validity of the model must be perfectly clear at all stages of the work. In principle, a spectrographic analysis is carried out in two steps.

1. The calibration function is estimated with the aid of standards of known composition.
2. The intensity of the unknown sample is determined and the calibration function used to calculate the proportion of that component to be determined in the sample.

Thus it is clear that the calibration function plays a very important part in analysis. A correct mathematical form of the calibration function would be the basis for further investigations along the lines discussed in the introduction.

In emission spectrographic work, a major cause of deviations from linearity in the calibration function is self-absorption. According to Boumans,<sup>2</sup> the effect of self-absorption can be described mathematically by using an exponential calibration function, including a part of the form

$$I'(t) = te^{a-bt}. \quad (1)$$

$I'(t)$  denotes the intensity of emission,  $t$  the concentration,  $a$  is a scaling constant and  $b$  is a constant that describes the degree of self absorption.

There is also always some background radiation, which can be included in the model by adding a constant,  $c$ , to give:

$$I''(t) = te^{a-bt} + c. \quad (2)$$

The effect of the background radiation is thus assumed to be purely additive.

As everyone who has worked with emission spectrography will know, all measurements of intensities according to (2) are subject to random variations. It has been considered realistic to assume that the measurements are approximately normally distributed for a given sample preparation with mean value  $I''(t)$  as given by (2), and a standard deviation which is proportional to that mean value. It is possible that the mean value for a given sample preparation should, sometimes, itself be regarded as a random variable describing the fluctuations between different preparations of the same sample. The variations between different preparations are, however, often small enough to be neglected. Isoformation methods for sample preparation are therefore assumed.

In principle, we have three different kinds of samples, *viz.* blanks, standards and unknowns. In order to simplify the formulae, we assume that the same number of runs is made on all samples. If so desired, the formulae can easily be modified, taking different numbers of runs into consideration. All the information that is needed for evaluation of an analysis is contained in the mean value of the intensities obtained from all runs on the sample. In the following, the word "intensity," and the notation  $I(t)$  will stand therefore for the mean intensity of all runs of preparations of the same sample.

As a result, we arrive at the following model for the measured intensity  $I(t)$ :

$$I(t) = (te^{a-bt} + c)(1 + \xi). \quad (3)$$

where  $a$ ,  $b$  and  $c$  denote non-negative constants and  $\xi$  is a normally distributed random variable with expectation zero and standard deviation  $\sigma$ , independent of  $t$ .

A prerequisite condition for all spectrographic analytical work is that matrix effects can be controlled in some way. This can be done either by employing some suitable form of isoformation or by using standards of approximately the same composition as the unknown samples to be analysed. In this work, we have been concerned with samples that have been isoformed by fusion or by sulphide precipitation, matrix effects thus being minimized. Consequently, we have neglected them in this work.

In order to ensure that a correct model is used, the model should be tested statistically.

#### *The error of a concentration determination*

In the preceding section, the equation for the calibration function was established and the importance of using a correct mathematical form was emphasized. That, however, does not imply that the calibration function must be correct in all respects. In fact, the coefficients  $a$ ,  $b$  and  $c$  are determined experimentally, their true values being unknown. Hence, an equation relating the error in the concentration determination to the magnitude of the coefficients and to the error made in their determination is of general interest and will now be derived.

Both the determination of the calibration function (standardization) and the analysis of the sample for the component to be determined, involve intensity measurements, and as all intensity measurements will vary randomly, the results of both steps will be subject to random errors. The true values of  $a$ ,  $b$  and  $c$  can never be determined but more or less good estimates of these parameters can be obtained. In the following discussion these estimates will be denoted by  $\hat{a}$ ,  $\hat{b}$  and  $\hat{c}$ , respectively.

The accuracy of the analyses will, on the one hand, depend on the values of the concentration  $t$  and  $a$ ,  $b$  and  $c$  and on the other, it will depend on how well these parameters can be estimated. Aiming at a quantitative treatment of the errors, we shall start by considering a sample having the (unknown) concentration  $t$ .

The measured intensity value is taken to be  $I(t)$  and the estimated concentration  $t^*$  is obtained as the least root of the equation

$$t^* \exp(\hat{a} - \hat{b}t^*) = I(t) - \hat{c}.$$

This equation may also be written

$$\left(\frac{t^* - t}{t} + 1\right) \exp\left[-\hat{b}t\left(\frac{t^* - t}{t}\right)\right] = (I(t) - \hat{c})/t \exp(\hat{a} - \hat{b}t). \quad (4)$$

If we denote the relative concentration error  $(t^* - t)/t$  by  $x$ ,  $\hat{b}t$  by  $\theta$  and the right-hand side of equation (4) by  $1 + \varepsilon$ , we have

$$(1 + x) \cdot \exp(-\theta x) = 1 + \varepsilon. \quad (5)$$

Up to this point, the only limitations are those imposed by the model and listed above. In order to obtain an explicit expression of the mean relative concentration error, which can be handled with standard statistical methods, it is advantageous that we assume that  $(1 - \theta)$  is not much less than unity and that  $\varepsilon$  is much less than unity. Anticipating the continuation of the discussion, we want to point out here that poor approximations (implying poor estimates of  $a$ ,  $b$ ,  $c$  and  $t$ ) show up as large errors of analysis. Since we are interested in obtaining small errors of analysis, such situations do not interest us.  $(1 + x) \exp(-\theta x)$  can then be approximated by its linear part and we can write

$$1 + (1 - \theta)x \approx 1 + \varepsilon; \quad x \approx \frac{\varepsilon}{1 - \theta}.$$

Substituting the expressions for  $x$ ,  $\theta$  and  $I(t)$  we get

$$\frac{t^* - t}{t} \sim \frac{\varepsilon}{1 - bt} \approx \frac{1}{1 - bt} \left\{ (a - bt) - (\hat{a} - \hat{b}t) + \frac{c - \hat{c}}{te^{a-bt}} + \xi \frac{te^{a-bt} + c}{te^{a-bt}} \right\}, \quad (6)$$

the last approximation implying that  $(a - \hat{a})$  and  $(b - \hat{b})t$  are small quantities. If we assume that  $(c - \hat{c})/te^{a-bt}$  and  $\xi(te^{a-bt} + c)/te^{a-bt}$  are both small quantities, we may automatically conclude that  $\varepsilon$  is small.

We want to point out that our principal interest lies in the *mean* relative concentration error. Thus, expression (6) for the relative concentration error is of little practical importance as the accuracies of a particular set of values of the parameter estimates and the value of the random variable  $\xi$  are generally unknown. But relationship (6) enables us to calculate the mean relative concentration error, which is of great practical importance.

In the following sections, the general method of solving the optimization problem is demonstrated with the aid of one situation, which is of particular importance in emission spectroscopy. In the last section, a few other situations of practical interest to the chemist are briefly discussed.

#### *Estimation of parameters a, b and c in the calibration function*

In this section, we are going to show how the empirical calibration function should be adapted to the true one. We have chosen to illustrate this by discussing a case with perfectly known concentrations in the standards and non-negligible background.

We estimate the mean background radiation  $c$  from one or several blank samples, i.e., samples in which the concentration of the component to be determined should equal zero. As estimate  $\hat{c}$  of  $c$  we take the mean intensity of the blanks. Samples



which are clearly contaminated, thus not fulfilling the condition of having zero concentration of the component, are discarded. Assuming that the number of blanks is  $m$ , we have a normally distributed estimate  $\hat{c}$ , having the mean value  $c$  and standard deviation  $c\sigma/\sqrt{m}$ .

Subsequently, parameters  $a$  and  $b$  are estimated from a number of standards with known concentrations of the component to be determined, in the following way. Let the concentrations of the standards (not all of which need be different) be denoted by  $t_1, t_2, \dots, t_n$  and let the corresponding mean intensities, which are obtained by measurement, be denoted by  $I_1, I_2, \dots, I_n$ . We reduce the observed intensities  $I_j$  by the estimated background  $\hat{c}$  and compute the "reduced intensities"  $I_j - \hat{c}$  ( $j = 1, 2, \dots, n$ ). The reduced intensities  $I_j - \hat{c}$  of the standard samples are observable random variables, which by using expression (3) may be written

$$I_j - \hat{c} = t_j e^{a-bt_j}(1 + \xi) + c\xi + c - \hat{c}. \quad (7)$$

As estimates of  $a$  and  $b$  we shall take the "maximum likelihood estimates," calculated for that statistical model which is obtained when  $c\xi + c - \hat{c}$  is deleted from (7). In practical applications,  $c\sigma$  and consequently  $c\xi$  are often negligible in relation to all the reduced intensities  $I_j - \hat{c}$ , and then the simplification of (7) is justified. If the background  $c$  is of the same order of magnitude as the reduced intensity of some standard but negligible in relation to all the other standards, then nothing is normally lost by exchanging this standard for one more blank and the exchange should be carried out.

Thus we calculate the estimates of  $a$  and  $b$  from the observations on  $I_j - \hat{c}$  in the simplified model

$$I_j - \hat{c} = t_j e^{a-bt_j}(1 + \xi) \quad (j = 1, \dots, n). \quad (8)$$

Let us introduce the notation

$$x_j = \ln(I_j - \hat{c}) - \ln t_j \quad (j = 1, \dots, n).$$

As  $\sigma$  is assumed to be small,  $\xi$  may well be substituted for  $\ln(1 + \xi)$ , and consequently each  $x_j$  is normally distributed with expectation  $a - bt_j$  and standard deviation  $\sigma$ . This means that we have arrived at a simple linear regression model. It is a standard statistical result that the maximum likelihood estimates  $\hat{a}$  and  $\hat{b}$  of  $a$  and  $b$  are given by the formulae

$$\hat{b} = \frac{\sum_{j=1}^n (t_j - \bar{t})(x_j - \bar{x})}{\sum_{j=1}^n (t_j - \bar{t})^2} \quad (9)$$

$$\hat{a} = \bar{x} - \hat{b}\bar{t},$$

where

$$\bar{t} = \frac{1}{n} \sum_{j=1}^n t_j \quad \text{and} \quad \bar{x} = \frac{1}{n} \sum_{j=1}^n x_j.$$

Equations for the estimation of  $a$  and  $b$ , yielding the estimates  $\hat{a}$  and  $\hat{b}$  have thus been derived. At the Geological Survey of Sweden these estimates have been computed routinely since December 1968, when this method replaced an earlier one.

*Calculation of the mean relative concentration error*

The mean relative concentration error, which forms the basis for judging the choice of standards, is defined as the square root of the mathematical expectation  $E(t^* - t)^2/t^2$ . This important quantity is now to be calculated. We derived earlier the expression (6) for the relative error  $(t^* - t)/t$ :

$$(t^* - t)/t \approx \frac{1}{1 - bt} \times \left\{ a - \hat{a} - (b - \hat{b})t + \frac{c - \hat{c}}{t \exp(a - bt)} + \frac{t \exp(a - bt) + c}{t \exp(a - bt)} \xi \right\}.$$

As the first step we will derive an approximation for  $a - \hat{a} - (b - \hat{b})t$ . Let  $\xi_1, \dots, \xi_n$  be independent random variables (corresponding to the intensities of the standards) with the same distribution as  $\xi$ . We have

$$\begin{aligned} a - \hat{a} - (b - \hat{b})t &= - \sum_{j=1}^n \left\{ \frac{1}{n} + \frac{(t_j - \bar{t})(t - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right\} \\ &\quad \times \ln \left\{ 1 + \left( 1 + \frac{c}{t_j \exp(a - bt_j)} \right) \xi_j + \frac{c - \hat{c}}{t_j \exp(a - bt_j)} \right\} \\ &\approx - \sum_{i=1}^n \left\{ \frac{1}{n} + \frac{(t_j - \bar{t})(t - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right\} \left\{ \left( 1 + \frac{c}{t_j \exp(a - bt_j)} \right) \xi_j + \frac{c - \hat{c}}{t_j \exp(a - bt_j)} \right\}, \end{aligned}$$

where the approximation is good provided that  $c - \hat{c}$  is small compared with each of the quantities  $t_j e^{a-bt_j}$ . After substitution of this approximation into  $(t^* - t)/t$ , the desired expectation is easily calculated. The expectation of the expression for  $(t^* - t)/t$  is now zero, and consequently the mean relative concentration error equals the standard deviation  $s(t)$  of  $(t^* - t)/t$ , within the accepted degree of approximation.

The standard deviation  $s(t)$  is obtained as the square root of the variance  $s^2(t)$ , which in turn can be expressed as the sum of two terms,

$$s^2(t) = s_1^2(t) + s_2^2(t), \tag{10}$$

where  $s_1^2(t)$  is the variance of  $\{a - \hat{a} - (b - \hat{b})t + (c - \hat{c})/te^{a-bt}\}/(1 - bt)$  and thus refers to the uncertainty in the determination of the calibration function, and  $s_2^2(t)$  is the variance of  $\xi\{te^{a-bt} + c\}/(1 - bt)te^{a-bt}$ , and thus refers to the random variation in intensity of the sample. Elementary statistical calculations show that

$$\begin{aligned} s_1^2(t) &= \frac{\sigma^2}{(1 - bt)^2} \left\{ \sum_{j=1}^n \left( 1 + \frac{c}{t_j \exp(a - bt_j)} \right)^2 \left( \frac{1}{n} + \frac{(t_j - \bar{t})(t - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right) \right. \\ &\quad \left. + \frac{c^2}{m} \left( \frac{1}{t \exp(a - bt)} + \sum_{j=1}^n \left( \frac{1}{n} + \frac{(t_j - \bar{t})(t - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right) \frac{1}{t_j \exp(a - bt_j)} \right)^2 \right\}, \tag{11} \end{aligned}$$

where  $m$  is the number of blank samples, and

$$s_2^2(t) = \frac{\sigma^2}{(1 - bt)^2} \left( 1 + \frac{c}{t \exp(a - bt)} \right)^2. \quad (12)$$

If we make and run  $k$  preparations of the same sample,  $s_2^2(t)$  should be divided by  $k$ :

$$s_2^2(t) = \frac{1}{k} \frac{\sigma^2}{(1 - bt)^2} \left( 1 + \frac{c}{t \exp(a - bt)} \right)^2. \quad (13)$$

#### RESULTS AND DISCUSSION

Before continuing the discussion, we feel that a few words about the preceding paragraphs are appropriate. The language used in them might seem prohibitively strange and complicated to the analyst. However, common statistical techniques are used and the important thing is to realize that statistics can provide the means for improving present analytical techniques. In order to accomplish the task, it is not necessary that the analyst penetrate in detail all the steps that led to the final results. Instead, he should establish a sufficiently accurate model in co-operation with the statistician, make use of the statistician's results and check and study the consequences from the chemical point of view.

1. The standard deviation  $s(t)$  (the mean relative concentration error) is a measure of the precision in the concentration determination, and  $s(t^*)$  can thus be used in daily routine as an approximate value for the precision of the analysis.

2. The mean relative concentration error also provides the analyst with means to optimize the precision by varying the standard concentration ( $t_i$ ) for a given number of blanks, standards and samples. Depending upon the concentration range in which maximum precision is desired, the optimal choice of standard concentrations will be different.

3. Finally the mean relative concentration error can be used to decide (a) how to attain maximum precision at a given cost and (b) how to attain a prescribed precision at minimum cost. This is accomplished by varying the number of blanks, standards and samples. By this, the economical aspects of an analysis are also taken into consideration. At least, the mean relative concentration error can be used to accomplish a reasonable distribution of the cost of analysis between blanks, standards and samples in a given situation.

A computer program, which allows variation of all parameters involved, has been designed and is now available at the Geological Survey of Sweden. On the one hand, the program can be used to compute the precision to be expected of the analyses that are made. On the other hand, it can also be used to study the effects of different choices of concentrations in the standards and of varying the number of runs of standards, blanks and samples.

In order to illustrate the practical consequences of our results, we have chosen as a model system the determination of aluminium in silicates by the tape method after isoformation by fusion. As approximate values of  $a$ ,  $b$  and  $c$  we have taken the following mean values obtained in practical analysis work:  $a = 3.20$ ,  $b = 0.01$ ,  $c = 0.015$ . The resulting curve is shown in Fig. 1. Then, we have used an electronic computer to calculate the mean relative error that would have resulted if those values of the constants  $a$ ,  $b$  and  $c$  had been obtained with various choices of blanks and

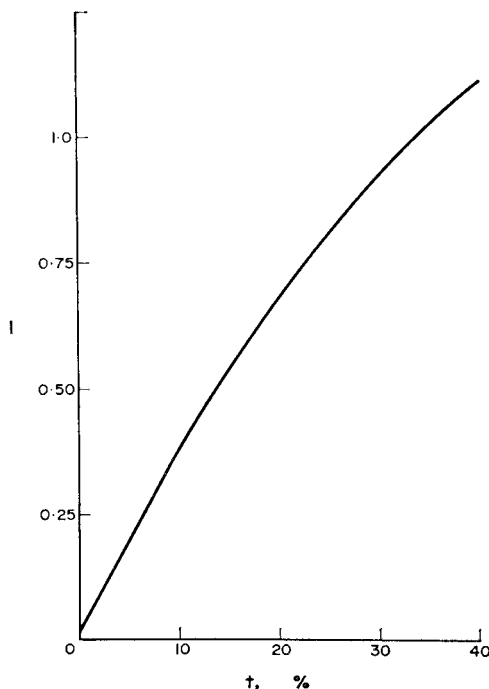


FIG. 1.—Calibration curve for determination of aluminium, showing the intensity  $I$  as a function of the concentration  $t$  of  $\text{Al}_2\text{O}_3$ .

standards. The standard deviation  $\sigma$  was assumed to be 1 for simplicity, the results being directly comparable for any value of  $\sigma$ , as long as the same value is used in all calculations. As can be seen from equations (11) and (13), the true value of the relative error can be obtained simply by multiplication by  $\sigma$ . In practice, an estimate of  $\sigma$  is substituted for  $\sigma$ . We make the assumption that a high precision is desired within the interval 0–25% of  $\text{Al}_2\text{O}_3$ , with the best precision around 12%.

We begin the study of the variance  $s^2(t) = s_1^2(t) + s_2^2(t)$  by an analysis of the first term  $s_1^2(t)$ , as given by (11), describing that loss of precision which is due to the error in the calibration curve.

To be able to estimate the three parameters  $a$ ,  $b$  and  $c$  we need at least one blank and two standards, which is the case in Fig. 2. This figure shows the curve  $s_1^2(t)$  for different values of the lower standard when the higher standard contains 30% of  $\text{Al}_2\text{O}_3$ . The optimum value of the lower standard is seen to be about 3% of  $\text{Al}_2\text{O}_3$ , but values between 1% and 7% of  $\text{Al}_2\text{O}_3$  can be used without greatly impairing the results. It is worth noticing how close to the blank the optimum value of the lower standard is.

When choosing standards, the following rule of thumb is useful: in most cases the minimum value of  $s_1^2(t)$  is obtained approximately at that concentration which is the arithmetic mean of the standards used. In Fig. 2 this can be verified, with an exception when the lower standard is as low as 0.2%. Considering this rule of thumb, it is not surprising that if the concentration of the higher standard is decreased and the concentration of the lower standard is adjusted so as to give the best possible variance curve, the minimum of the resulting curve will shift to lower values of  $t$  and at the

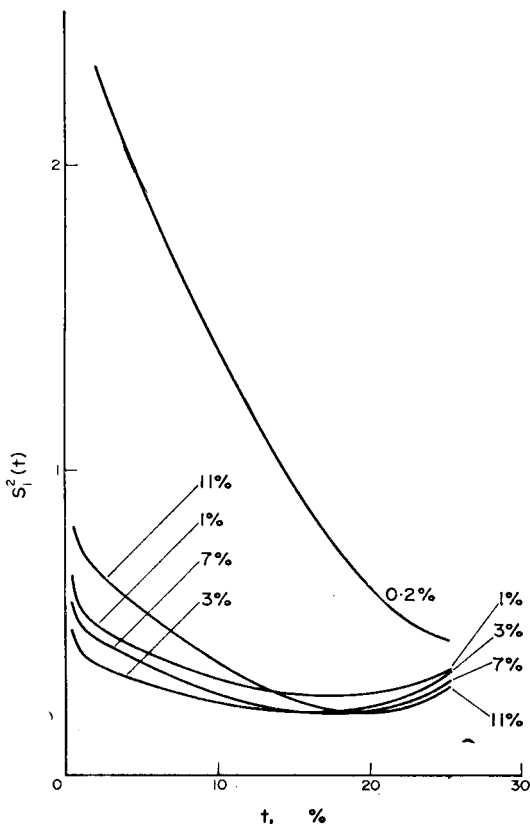


FIG. 2.—The relative mean-square concentration error  $s_1^2(t)$  due to the uncertainty in the determination of the calibration function as a function of the concentration of  $\text{Al}_2\text{O}_3$ . Two standards are used, one at 30%  $\text{Al}_2\text{O}_3$ , while the concentration of the lower standard is varied.

same time this minimum value of the curve will be lower, as shown in Fig. 3. However, as the concentrations of the standards approach each other, the variance curve will rise much faster for both high and low  $t$ -values. Using only two standards and a blank, it is then possible to optimize the variance curve for a limited range of concentrations, but the best overall results will be obtained when the concentration of the higher standard is as high as possible, considering that the model should still be valid at that concentration.

In Fig. 4,  $s_1^2(t)$  is plotted for some sets of 3 standards. Curve I shows the result for 7, 12 and 17% of  $\text{Al}_2\text{O}_3$ , the standard concentrations originally used in the determination of aluminium at SGU. Curve II shows the effect of symmetrically widening the range of standards—the standards used are 3, 12 and 21%. Still more separated are the standards generating curve III—two standards at 3% and one standard at 30% of  $\text{Al}_2\text{O}_3$ . All three curves have approximately equal minima around 12% but there is a remarkable difference in their shapes, showing that a clever choice of standards may substantially improve the analysis for both low and high concentrations. Comparison with Fig. 2 shows that even with two standards we may get a

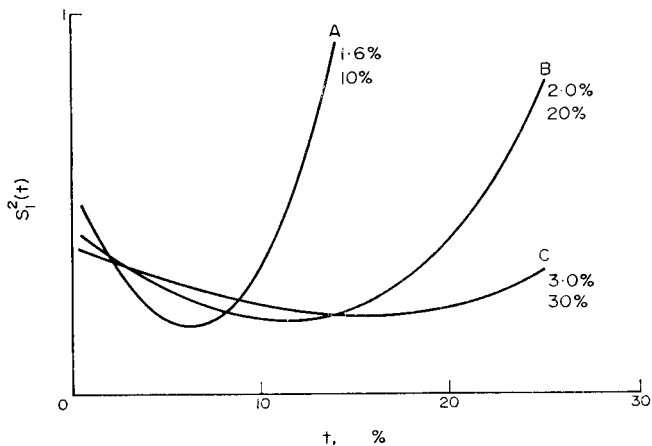


FIG. 3.— $s_1^2(t)$  as a function of the concentration  $t$  for different concentrations in two standards.

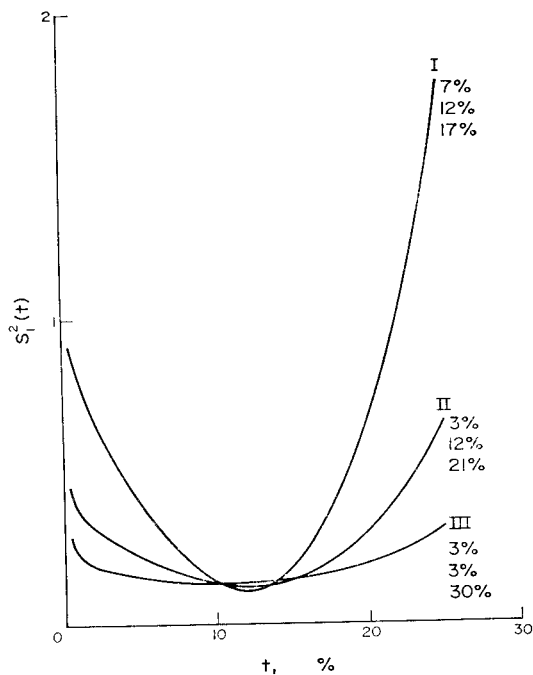


FIG. 4.— $s_1^2(t)$ —due to the uncertainty in the determination of the calibration function—for some different sets of three standards, as a function of  $t$ .

better result over most of the interval 0–25% than with the three standards 7, 12 and 17%.

In Fig. 5,  $s^2(t) = s_1^2(t) + s_2^2(t)$  is plotted in such a way that the contribution from each of the two terms  $s_1^2(t)$  and  $s_2^2(t)$  can be seen. Furthermore  $s_1^2(t)$  is separated into two terms, describing the uncertainty due to estimation of  $a - bt$  and  $c$  respectively. The small area for low concentrations describes the contribution from the

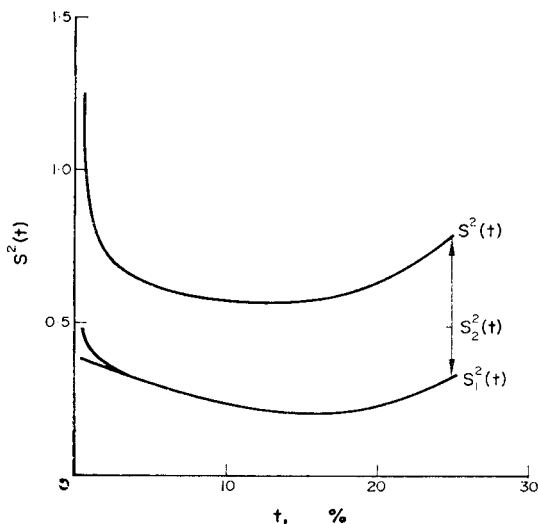


FIG. 5.— $s^2(t) = s_1^2(t) + s_2^2(t)$  for a blank and two standards at 3% and 30% of  $\text{Al}_2\text{O}_3$ , for  $0.5\% \leq t \leq 25\%$ . The upper branch of  $s_1^2(t)$  results when the uncertainty due to estimation of  $c$  is taken into consideration; in the lower branch this contribution is eliminated.

estimation of the background  $c$ . One blank and two standards, at 3 and 30% of  $\text{Al}_2\text{O}_3$  are assumed.

The figure shows a rapid increase in  $s_2^2(t)$  when  $t$  tends to zero, implying that the relative error must be expected to be large for very low values of  $t$ . But that does not imply that the absolute error of analysis is large.

The rest of this section will be devoted to the derivation of another rule of thumb, this time for deciding what is the most reasonable proportion between the number  $n$  of standards and the number  $k$  of preparations of a sample.

The answer depends on the number of samples that should be analysed at the same time, and consequently with the same estimates of  $a$ ,  $b$  and  $c$ . Let this number be  $N$ . It also depends on the cost for running a standard or a sample preparation. Let these costs be denoted by  $C_1$  and  $C_2$  respectively. We assume that the uncertainty due to estimated background is small, as is the case with aluminium, so that there is no reason for running more than one blank. Suppose also that the  $N$  samples all have concentrations of about 12% of  $\text{Al}_2\text{O}_3$ .  $s_1^2(t)$  is then approximately inversely proportional to the number  $n$  of standards and  $s_2^2(t)$  is inversely proportional to the number  $k$  of sample preparations. Consequently the variance  $s^2(t)$  for  $t \approx 12\%$  may be written  $s^2 \approx A_1/n + A_2/k$ , where the proportionality constants  $A_1$  and  $A_2$  may be estimated from Fig. 5.

The total cost for running the  $n$  standards and the  $k$  preparations of each of the  $N$  samples is  $C_1n + C_2Nk$ . It is reasonable that the analyst either wants to minimize the total cost at a prescribed precision of analysis or to maximize the precision of the analysis at a prescribed cost. In any case the optimal proportion between  $n$  and  $k$  is obtained by minimizing the product

$$\left(\frac{A_1}{n} + \frac{A_2}{k}\right) \cdot (C_1n + C_2Nk)$$

Differentiation shows that the optimal value of  $n/k$  is

$$(n/k)^2 = \frac{A_1 C_2}{A_2 C_1} \cdot N.$$

For aluminium it can be seen from Fig. 5 that  $A_1$  and  $A_2$  are approximately equal. If the costs for standards and samples are equal, *i.e.*  $C_1 = C_2$ , we obtain the simpler formula  $n/k = \sqrt{N}$ .

If we make only one run of each sample we may for instance conclude that we should use more than two standards at least when the number  $N$  of samples to be analysed is larger than 6. Of course we cannot use less than two standards whatever the value of  $N$ .

#### CONCLUSION

The discussion presented in this paper is based upon a calibration function that is used at present at the Geological Survey of Sweden. It is, however, appropriate to mention that preliminary investigations indicate that better agreement over a larger range of intensities and concentrations can be obtained with a calibration function of the form  $I(t) = k_1 t e^{k_2 I(t)}$  where  $k_1$  and  $k_2$  denote constants. The extent of self-absorption is dependent on the concentration of the element in question in the plasma of the spark gap. As the intensity is a better measure of the number of atoms in the spark gap than is the concentration of the sample, the physical basis of the new model is better than that of the old one. Statistical tests of the models will show which one is to be preferred.

As a final remark, we once more want to emphasize that the concepts which we have put forward in this paper are useful not only in emission spectroscopy but in all cases when an accurate model can be established.

As one further example we may mention absorption photometry where, according to Beer's law, plotting of absorbance *vs.* concentration should produce a straight line. Since most photometers are linear with respect to transmittance, however, the best accuracy in absorbance can be expected at an absorbance = 0.434 (corresponding to a transmittance = 36.8%). The choice of standards is again an optimization problem, which can be solved by a technique similar to the one we have used.

In X-ray fluorescence analyses, for instance in steel-works, the standardization is often performed with a great number of carefully analysed samples taken from production. This is a very expensive procedure. There is a need to optimize the standardization work by choosing standard samples of the most suitable composition. When it is possible to establish a mathematical expression of the calibration function in X-ray fluorescence the technique presented above could be helpful in making the best choice of standards. That will probably result in a demand for synthetic standard samples, as the compositions would be different from real steel samples.

Even in microprobe X-ray analyses the choice of standards might, in many cases, be improved by using mathematical statistical methods.

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**Zusammenfassung**—Als Hilfsmittel zur Wahl der Standardkonzentrationen bei der Emissionsspektroskopie wird ein Verfahren angegeben, das sich der mathematischen Statistik bedient. Das Verfahren wird auf die Analyse isoformierter Proben nach der Bandmethode angewandt. Einige andere mögliche Anwendungen (z.B. Röntgenfluoreszenz, Absorptionsphotometrie) werden kurz diskutiert.

**Résumé**—On présente une voie d'accès utilisant les statistiques mathématiques pour aider au choix de concentrations standard dans la spectroscopie d'émission. On applique la méthode à l'analyse d'échantillons "isoformés" par la méthode de bande. On discute brièvement de quelques autres applications possibles (par exemple, fluorescence de rayons X, photométrie d'absorption).

#### REFERENCES

1. A. Danielsson, *Spectrochemical Analysis for Geochemical Purposes, XIII Colloquium Spectroscopicum Internationale*. Hilger, London, 1968.
2. P. W. J. M. Boumans, *Theory of Spectrochemical Excitation*. Hilger & Watts, London, 1966.

## SHORT COMMUNICATIONS

### AAS-Bestimmung von Natrium und Kalium in den hochschmelzenden Metallen Wolfram und Molybdän

(Eingegangen am 15. Januar 1971. Angenommen am 28. April 1971)

DIE TECHNOLOGISCHEN EIGENSCHAFTEN und das Rekristallisationsverhalten der hochschmelzenden Metalle Wolfram und Molybdän werden in außerordentlich starkem Maße durch geringste Fremdstoffspuren beeinflusst. In der Glühlampenindustrie werden dazu dem pulvermetallurgisch gewonnenen Wolfram zur Erzielung einer sog. Langkristallstruktur kleinste Mengen an Kalium, Aluminium und Silizium zugegeben. Die Konzentration dieser Dopsbstanzten beträgt dabei weniger als 0,01 %.<sup>1-3</sup>

In der analytischen Chemie hat sich die Atom-Absorptions-Spektroskopie in vielen Fällen als eine störungsfreie Analysen-Schnellmethode bewährt und dabei eine besondere Verbreitung auf dem Gebiet der Spurenanalyse erfahren. Für den analytischen Nachweis der Dopsbstanzten in Wolfram und Molybdän sollte sie daher ein schnelles und zuverlässiges Bestimmungsverfahren sein.

Als erster Schritt zur Einführung der Atom-Absorptions-Spektroskopie in die analytische Bestimmung der Dopsbstanzten sollte daher ein Verfahren zur Bestimmung der Alkalimetalle Kalium und Natrium, das stets als Begleitstoff auftritt, in Wolfram und Molybdän erprobt werden.

In der Literatur ist in einer Vielzahl von Arbeiten<sup>4</sup> die Bestimmung von Natrium und Kalium mit Hilfe der Atom-Absorptions-Spektroskopie untersucht worden. Die Mehrzahl der Arbeiten befaßt sich jedoch mit dem Nachweis der Alkalimetalle bei der Silikat-, Zement- oder Wasseranalyse bzw. mit dem Nachweis in der Anwendung auf medizinische und biologische Problemstellungen, nicht jedoch mit der Bestimmung der Alkalimetalle in Gegenwart von größeren Schwermetallmengen.

#### EXPERIMENTELLER TEIL

##### Apparatur

Die Untersuchungen wurden mit einem kommerziellen Atom-Absorptions-Spektralphotometer, Modell 303 der Fa. Perkin-Elmer, durchgeführt. Die Versuchsdaten sind im einzelnen in der Tabelle I zusammengestellt.

##### Reagentien und Lösungen

Die verwendeten Chemikalien entsprachen den folgenden Reinheitsgraden:

Wolfram, zonengereinigt durch Elektronenstrahlsschmelze

Molybdän, MoO<sub>3</sub>, p.a. (Merck)

Wasserstoffperoxid 30% ig, Selectipur (Merck)

Weinsäure, p.a. (Merck)

Natrium-, Kalium- und Caesiumchlorid, Suprapur (Merck)

Ammoniaklösung Suprapur (Merck).

##### Vorgang

Die fein pulverisierte Probe ( $1000 \pm 10$  mg auf 0,1 mg genau gewogen) wird mit 1 g Citronensäure in 10 ml 30% igem Wasserstoffperoxid vorsichtig gelöst und, wenn Wolfram anwesend ist, erwärmt bis die Lösung klar wird. Sie wird in einem 50-ml Meßkolben überführt, 5 ml einer 10-mg/ml Caesiumlösung werden zugegeben, und bei  $20 \pm 2^\circ$  mit dest. Wasser aufgefüllt. Die Extinction  $E_x$  wird bei 589,0 nm (Na) oder 766,5 nm (K) gemessen. Die Extinction eines Nullstandards,  $E_0$ , oder, in Falle Molybdäns, einer Blindprobe,  $E_b$  wird gemessen, und die Extinction  $E = E_x - E_0$  bzw.  $E = E_x - E_b$  berechnet. Die Konzentration wird aus einer stets überprüften Eichkurve abgelesen.

#### VERSUCHSERGEBNISSE

Zur Ermittlung des linearen Absorptionsbereiches wurde zunächst das Absorptionsverhalten reiner, wäßriger Natrium- und Kaliumlösungen untersucht. Es zeigte sich, daß die Extinktion in einem Arbeitsbereich der Alkalikonzentration von 0,1  $\mu\text{g/ml}$  bis zu 15  $\mu\text{g/ml}$  einen linearen Verlauf mit der Konzentration aufweist.

TABELLE I.—VERSUCHSBEDINGUNGEN

|                      |   |
|----------------------|---|
| Spektrometer         | Perkin-Elmer 303                                |
| Schreiber            | Hitachi 165                                     |
| Hohlkathodenlampen   | Intensitron                                     |
| Wellenlängen         | Na: $\lambda$ 589,0 nm<br>K: $\lambda$ 766,5 nm |
| Spaltbreite          | Na: 0,3 mm<br>K: 1 mm                           |
| Spektrale Bandbreite | Na: 0,47 nm<br>K: 1,36 nm                       |
| Brenngas             | Acetylen  |
| Druck                | 0,60 atü  |
| Strömungsgeschw.     | 4 Liter/min.                                    |
| Oxydans              | Luft  |
| Druck                | 2 atü   |
| Strömungsgeschw.     | 20 Liter/min.                                   |
| Sprühgeschwindigkeit | 2,5 ml/min.                                     |

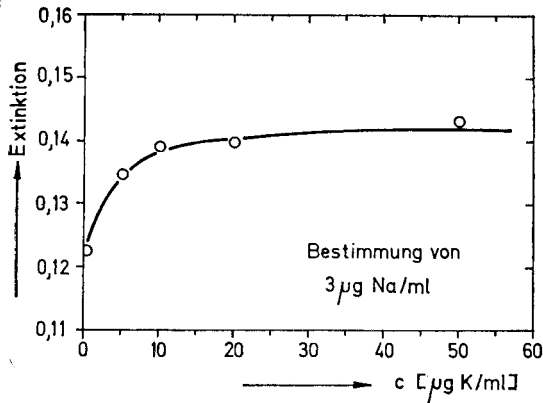
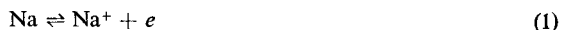


ABB. 1.—Beeinflussung der Natrium-Absorption durch Kalium.

Die Literaturangaben<sup>5-10</sup> über die gegenseitige Beeinflussung der Alkalimetalle bei der Atom-Absorptions-Spektralanalyse sind oft widersprüchlich. Der Einfluß der Alkalimetalle aufeinander wurde daher experimentell überprüft. Es zeigt sich, daß eine Beeinflussung der K-Absorption durch Natrium nicht stattfindet, wohl aber eine Verstärkung der Na-Absorption (Abb. 1) durch Kalium zu beobachten ist. Ursache dieser Interferenz ist das Ineinandergreifen der Ionisationsgleichgewichte der Alkalimetalle in der Flamme



Durch die freie Elektronenkonzentration des leichter ionisierbaren Metalles wird die Ionisation des schwerer ionisierbaren Metalles zurückgedrängt und dadurch die für den Nachweis nötige Atomkonzentration dieses Metalles erhöht. Dieser Mechanismus läßt sich ausnutzen, wobei durch Zugabe eines dritten, noch leichter ionisierbaren Metalles—hier Caesium—gleichzeitig die Absorption der beiden anderen Alkalimetalle verstärkt und die gegenseitige Störung beseitigt wird.

Dabei zeigt sich (Abb. 2), daß der Einfluß des Caesiumzusatzes wesentlich stärker auf die Absorption des Kaliums als auf diejenige des Natriums wirkt.

Zur Untersuchung des Einflusses der Matrixelemente (W, Mo) auf die Absorption der Alkalimetalle wurden bei konstant gehaltener Alkalikonzentration den Probelösungen ansteigende Mengen der Matrixelemente zugesetzt. Die Ergebnisse sind graphisch in der Abb. 3 dargestellt. Während Wolfram keinen Einfluß auf das Absorptionsverhalten der Alkalimetalle ausübt, wurde eine recht starke Erhöhung der Absorption des Kaliums durch die Gegenwart von Molybdän beobachtet.

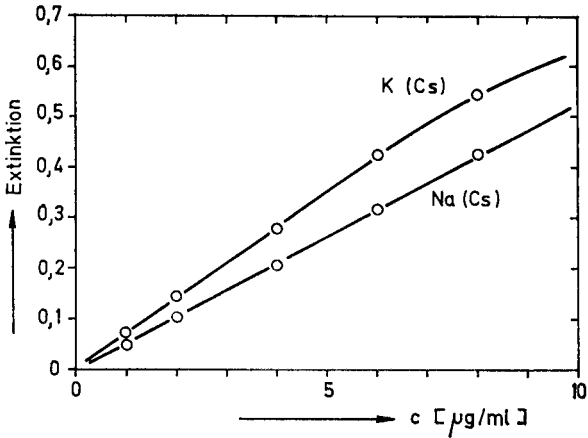


ABB. 2.—Atom-Absorption von Natrium und Kalium in Gegenwart von Caesium.

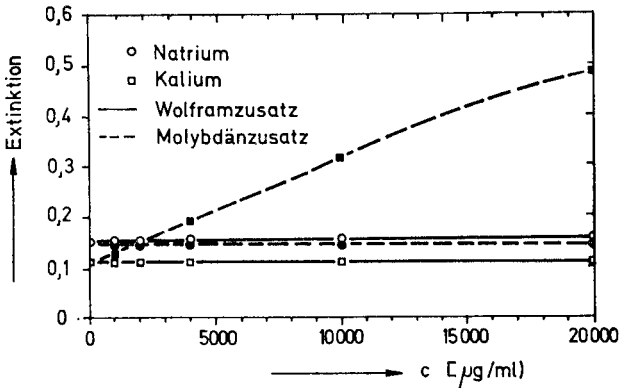


ABB. 3.—Einfluß von Wolfram und Molybdän auf die Atom-Absorption von Natrium und Kalium.

Da im Gebiet der untersuchten Wellenlängen weder elementares Molybdän noch Molybdänoxide eine Absorption aufweisen, läßt sich diese beobachtete Störung der Kaliumabsorption in Gegenwart von Molybdän zunächst nur durch einen Streueffekt der Hohlkathodenstrahlung an den Partikeln der leichtflüchtigen Molybdänoxide, wie auch früher bei der Rheniumbestimmung<sup>11</sup> diskutiert, erklären. Zur Elimination dieser Störung muß bei der Analyse die Matrixkonzentration entweder konstant gehalten werden oder die Analyse muß nach der Additionsmethode durchgeführt werden.

Ferner wurde der Einfluß der ebenfalls in Wolfram und Molybdän gegenwärtigen Metalle Calcium und Aluminium auf die Absorption der Alkalimetalle untersucht. Eine wesentliche Beeinflussung wurde jedoch selbst bei einem großen Überschuß von Calcium und Aluminium (500–1000 fach) nicht beobachtet, wie auch aus Tab. II ersichtlich ist.

Als untere Nachweisgrenze für die Alkalibestimmung wurde eine Konzentration von 0,02  $\mu\text{g}$  Na bzw. K/ml ermittelt. Für die durch die Bedingung von 1% Absorption gegebene sichere Nachweisgrenze ergab sich ein Wert von 0,05  $\mu\text{g/ml}$ . Bei einer Probeneinwaage von 2000 mg/100 ml erhält man damit eine untere Nachweisgrenze von 3 ppm Na bzw. K in W bzw. Mo.

Die Ermittlung der relevanten Verfahrensdaten erfolgte mit Hilfe eines Computerprogrammes nach Gottschalk.<sup>12</sup> Dabei wurde für den funktionellen Zusammenhang zwischen der Konzentration des zu bestimmenden Elementes und dem Meßwert die Gültigkeit einer dem Lambert-Beerschen Gesetz analogen Beziehung  $E = k \cdot c$  angenommen, wobei  $E = \text{Extinktion} = 2 - \log D$  ( $D = \text{Durchlässigkeit}$ ) bzw.  $= 2 - \log(100 - A)$  ( $A = \text{Absorption}$ ),  $k = \text{Verfahrenskoeffizient}$  in

TABELLE II.—EINFLUSS VON CALCIUM UND ALUMINIUM  
AUF DIE ABSORPTION VON Natrium UND Kalium IN  
GEGENWART VON CAESIUM (1000  $\mu\text{g Cs/ml}$ )

| Na<br>$\mu\text{g/ml}$ | K<br>$\mu\text{g/ml}$ | Ca<br>$\mu\text{g/ml}$ | Al<br>$\mu\text{g/ml}$ | Extinktion<br>$E$ |
|------------------------|-----------------------|------------------------|------------------------|-------------------|
| 1                      | —                     | —                      | —                      | 0,0788            |
| 1                      | —                     | 1000                   | —                      | 0,0868            |
| —                      | —                     | 1000                   | —                      | 0,0088            |
| 1                      | —                     | —                      | —                      | 0,0788            |
| 1                      | —                     | —                      | 1000                   | 0,0858            |
| —                      | —                     | —                      | 1000                   | 0,0083            |
| —                      | 2                     | —                      | —                      | 0,1073            |
| —                      | 2                     | 1000                   | —                      | 0,1082            |
| —                      | —                     | 1000                   | —                      | 0,0044            |
| —                      | 2                     | —                      | —                      | 0,1073            |
| —                      | 2                     | —                      | 1000                   | 0,1014            |
| —                      | —                     | —                      | 1000                   | 0,0057            |

$\text{ml} \cdot \mu\text{Mol}^{-1}$ ,  $C$  = Konzentration in  $\mu\text{Mol} \cdot \text{ml}^{-1}$  bedeutet. Für die praktische Auswertung werden Beziehungen der Form  $C = k_1 \cdot E$  bzw.  $C = k_0 + k_1 \cdot E + k_2 E^2$  die Abweichungen vom Idealgesetz berücksichtigen, berechnet. Der Verfahrenskoeffizient muß durch Eichmessungen bestimmt werden und gilt nur in einem mehr oder minder begrenzten Konzentrationsbereich bei genauer Einhaltung definierter Arbeitsschritte und Versuchsbedingungen. In der Tabelle III sind die Verfahrensdaten kurz zusammengefaßt.

TABELLE III.—VERFAHRENSDATEN ZUR AAS-BESTIMMUNG VON Natrium UND  
Kalium IM BEREICH 0,01–0,1  $\text{mm}$

|  | in Wolfram                        |                                | In Molybdän   |                                |
|--|-----------------------------------|--------------------------------|---|--------------------------------|
|  | Natrium                           | Kalium                         | Natrium   | Kalium                         |
| Berechnungs-<br>funktion   | $C = k_1 \cdot E + k_2 \cdot E^2$ |                                | $C = k_0 + k_1 \cdot E + k_2 \cdot E^2$ $c = k_1 \cdot E + k_2 \cdot E$ |                                |
| Verfahrens-<br>konstanten,<br>$\text{ml} \cdot \mu\text{Mol}^{-1}$ | $k_1 = 0,299$<br>$k_2 = 0,064$    | $k_1 = 0,299$<br>$k_2 = 0,226$ | $k_0 = 1,5 \times 10^{-3}$<br>$k_1 = 0,401$<br>$k_2 = 0,166$            | $k_1 = 0,307$<br>$k_2 = 0,176$ |
| Standard-<br>abweichung,<br>$\mu\text{Mol} \cdot \text{ml}^{-1}$   | $0,64 \times 10^{-3}$             | $0,47 \times 10^{-3}$          | $0,57 \times 10^{-3}$   | $0,36 \times 10^{-3}$          |
| Bestimmungs-<br>grenze,<br>$\mu\text{Mol} \cdot \text{ml}^{-1}$    | 0,003 <sub>4</sub>                | 0,002 <sub>4</sub>             | 0,003   | 0,008                          |

### Schlußfolgerung

Die Ergebnisse der vorliegenden Untersuchungen zeigen, daß die Atom-Absorptions-Spektroskopie mit ausreichender Genauigkeit für die Analyse der Dopsbstanzten Kalium und Natrium in Wolfram und Molybdän eingesetzt werden kann. Die Nachweisempfindlichkeit liegt dabei in der üblichen Größenordnung, wie sie u.a. auch im Handbuch der Fa. Perkin-Elmer angegeben wird. Da die Atom-Absorptions-Spektroskopie lediglich das Auflösen der metallischen Probe in einem geeigneten Lösungsmittel und anschließende Messung der Absorption erfordert, hat man ein einfaches Analysenschnellverfahren zur Hand, um Natrium und Kalium in Wolfram und Molybdän bis zu Werten von einigen ppm herab zu bestimmen.

Anerkennung—Für die sorgfältige Durchführung der Analysen danke ich Frau E.U. Stamer.

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**Zusammenfassung**—Es wird über die Ergebnisse der AAS-Bestimmungen von Natrium und Kalium in Anwesenheit größerer Mengen von Wolfram und Molybdän berichtet. Die wechselseitige Störung der Alkalimetalle wird durch Zusatz von Caesium überwunden. Wolfram stört nicht, während die Störung durch Molybdän, die proportional seiner Menge ist, kontrolliert werden kann, indem man das Gewicht der Probe konstant hält. Die AAS-Bestimmung ist also ohne vorhergehende Trennung direkt durchführbar. Die Empfindlichkeit für 1% Absorption beträgt 0,05  $\mu\text{g/ml}$  des Alkalimetals.

**Summary**—Results for the atomic-absorption behaviour of sodium and potassium in the presence of large amounts of tungsten and molybdenum are reported. The mutual interference of the alkali metals is overcome by the addition of caesium. Of the matrix-elements tungsten showed no interference, while molybdenum had a proportional interference effect, which can be overcome by keeping the specimen weight at a constant value. Thus, AAS can be applied for the determination of K and Na in W and Mo without prior separation procedures. The sensitivity found for 1% absorption was 0,05  $\mu\text{g}$  of alkali/ml of solution.

**Résumé**—On rapporte des résultats pour le comportement à l'absorption atomique du sodium et du potassium en la présence de grandes quantités de tungstène et de molybdène. L'interférence mutuelle des métaux alcalins est surmontée par l'addition de caesium. Des éléments de la matrice, le tungstène ne montre pas d'interférence, tandis que le molybdène a un effet d'interférence proportionnel, que l'on peut surmonter en maintenant le poids de spécimen à une valeur constante. Ainsi, l'AAS peut être appliqué au dosage de K et Na dans W et Mo sans techniques de séparation préalables. La sensibilité trouvée pour 1% d'absorption a été de 0,05  $\mu\text{g}$  d'alcali/ml de solution.

#### LITERATUR

1. T. Millner, *Acta Tech. Acad. Sci. Hung.*, 1957, **17**, 67.
2. H. L. Spier, *Philips Res. Rept.*, 1962, Nr. 3.
3. T. Millner, *Acta Tech. Acad. Sci. Hung.*, 1965, **50**, 203.
4. s. Literaturzusammenstellung in: W. Slavin, *Atomic Absorption Spectroscopy*. Interscience, New York, 1968; und J. Ramirez-Muñoz, *Atomic Absorption Spectroscopy*. Elsevier, Amsterdam, 1968.
5. H. Samui und N. Pace, *Appl. Spectry*, 1966, **20**, 135.
6. J. W. Robinson, *Anal. Chim. Acta*, 1960, **23**, 458.
7. E. Althaus, *N. Jahrbuch. für Mineralogie, Monatshefte* 1966, 159.
8. T. Takeuchi und M. Suzuki, *Talanta*, 1964, **11**, 1391.
9. M. J. Fishman, *Atomic Absorption Newsletter*, 1966, **5**.
10. C. A. Baker und F. J. W. Garton, *UKAEA-AERE-R* 3490, 1961.
11. G. M. Neumann, *Talanta*, 1971, **18**, 955.
12. G. Gottschalk, *Z. Anal. Chem.*, 1968, **241**, 39.

---

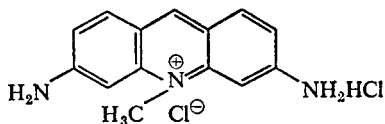
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### New methods for the detection of carboxylic acid groups in organic compounds, with acriflavine

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ONLY a few qualitative tests are available<sup>1</sup> for the detection of the carboxylic acid group in organic compounds. The confusion and difficulties are encountered by students in using the classical sodium bicarbonate and litmus paper tests for carboxylic acids. Certain other reported methods<sup>1</sup> lack simplicity and rapidity. The present communication describes two simple, reliable, rapid, and new colour tests for the carboxylic acid group, involving the use of acriflavine.

Acriflavine (euflavine, tryptaflavine) is a brownish-red, water-soluble (partly alcohol-soluble) crystalline dye, giving on dilution a yellow or yellowish-orange solution with green fluorescence. Chemically, it is not a single entity but a mixture of the monohydrochlorides of 2,8-diaminoacridine and 2,8-diamino-10-methylacridinium chloride.<sup>2,3</sup> However, it is generally represented by the formula:



Very limited work has so far been done on the chemical reactions<sup>4-7</sup> of acriflavine. In 1932, Udall<sup>5</sup> reported the reaction of acriflavine with nitrous acid (generated *in situ* from sodium nitrite and hydrochloric acid) to give a violet colour. The reaction has been re-investigated and modified, and has been made applicable to the detection of the carboxylic acid group in organic compounds. In the modified reaction, nitrous acid is liberated by the reaction of a carboxylic acid and sodium nitrite. The test is highly specific for carboxylic acids; other acidic compounds, viz. phenols, thiophenols, enols (*e.g.*, ascorbic acid and acetoacetic ester), acid imides, sulphonamides, and sulphonic acids (freshly prepared and unoxidized) do not respond to this test. Aminosulphonic acids (such as sulphanilic acid) also behave negatively to this test. Unsubstituted sulphonic acids and phenol sulphonic acids, however, interfere.

A further reaction has been developed for the detection of carboxylic acid with acriflavine. The reaction involves the treatment of the acid compound with acriflavine in presence of potassium chromate, when a yellow to brownish-yellow precipitate is formed which dissolves on heating or on adding acetone. This reaction too has been found specific for carboxylic acids. The applications and limitations of the test are almost the same as in the case of acriflavine/sodium nitrite test. However, this test is not applicable to those carboxylic acids which are practically insoluble in water. Besides unsubstituted and phenol sulphonic acids, enols also interfere in this test.

The acriflavine/sodium nitrite test has also been applied for the selective detection of nitrite ion (in inorganic compounds) in presence of a large number of foreign anions and cations.

## EXPERIMENTAL

### Reagents

**Acriflavine solution.** A 0.1% w/v solution in water, prepared from B.P.C. grade reagent. This solution was used for the detection of the carboxylic acid group in organic compounds. A similar 0.1% w/v solution in acetone was used in the detection of inorganic nitrites.

**Potassium chromate solution.** A 1% w/v solution in water.

**Sodium nitrite.**

**Organic acidic compounds.** Various analytical-grade aliphatic and aromatic carboxylic acids, phenols, thiophenols, enols, sulphonic acids, sulphonamides, and acid imides.

### Procedures for the detection of carboxylic acid group

**Acriflavine/sodium nitrite test.** Mix 1 or 2 drops (if liquid) or ~50 mg of powdered (if solid) test compound with 5 ml of water, and warm the mixture slightly (but do not boil). To this, add a spatula end (about 20 mg) of sodium nitrite and 1 or 2 drops of 0.1% aqueous acriflavine solution. A positive response is indicated by the appearance of a violet or purple colour.

The following acids were tested, and all gave positive results: formic, acetic, propionic, malonic, glutaric, adipic, succinic, malic, maleic, citric, tartaric, pyruvic, benzoic, phenylacetic, phthalic, fumaric, salicylic, acetylsalicylic, sulphosalicylic, chloroacetic, dichloroacetic, trichloroacetic, *p*-nitrobenzoic, and ethylenediaminetetra-acetic.

The intensity of the colour produced in the test was maximum in the case of aliphatic acids, fairly intense for unsubstituted aromatic acids, and medium to low for substituted aromatic acids.

**Acriflavine/potassium chromate test.** Take about 3 ml of 0.1% acriflavine solution, and add to it 3 drops of 1% potassium chromate solution followed by a few drops of the test compound (liquid or aqueous solution). Appearance of a yellow to brownish-yellow precipitate indicates the presence of a carboxylic acid group. The precipitate dissolves on heating or on adding a few ml of acetone.

### Procedure for the detection of nitrite ion

To 1 ml of the test solution, add 1 drop of concentrated hydrochloric acid and 1 drop of 0.1% acetone solution of acriflavine. A positive response is indicated by the appearance of a violet or

purple colour. The limit of detection is 25  $\mu\text{g/ml}$ . Amounts of nitrite lower than 25  $\mu\text{g/ml}$  give a red colour. Save for iodide, no other (out of 100 ions tested) anion or cation caused any interference.

## RESULTS AND DISCUSSION

### *Influence of pH on the dye and its reactions*

A neutral, dilute aqueous or alcoholic solution of acriflavine dye is yellow or yellowish-orange, but the colour is dependent on the pH.<sup>4</sup> The sharpest development of the colour in the sodium nitrite/acriflavine test was found to be in the range of pH 2-3. However, a fair detection can also be made up to pH 4. The maximum pH permissible for the acriflavine/potassium chromate test is  $\sim 6$ .

### *Effect of dye concentration*

The concentration of dye is very important. Higher concentrations of the dye ( $>0.2\%$  w/v) seriously hinder the brightness of the violet colour produced in the sodium nitrite/acriflavine test; instead, a reddish-brown or dirty violet colour is observed. Best colour development takes place at dye concentration less than 0.15% w/v. Concentrated dye solutions ( $>0.5\%$  w/v) give a yellow precipitate with potassium chromate even without the addition of the acid compound, hence making the acriflavine/potassium chromate test impossible. At lower concentrations ( $<0.2\%$  w/v), there is no such interference, and the test can be easily performed.

### *Interferences*

In both the tests for carboxylic acid group, unsubstituted sulphonic acids and phenol sulphonic acids (owing to their large  $K_a$  values) cause interference. Enols interfere in the acriflavine/potassium chromate test. Amino-substituted sulphonic acids (such as sulphanilic and metanilic acids), however, do not give this test, and so cause no interference. This is owing to their existence as zwitter-ions (e.g.  $^+\text{H}_3\text{N}-\text{C}_6\text{H}_4-\text{SO}_3^-$ ). The salts of organic bases do not interfere with the sodium nitrite/acriflavine test. The following salts were tried, and all gave negative results: aniline hydrochloride, aniline sulphate, methylamine hydrochloride, guanidine hydrochloride, and 2,6-diamino-3-phenylazopyridine monohydrochloride (pyridium). However, serious interference by these salts was observed in the acriflavine/potassium chromate test.

### *Negative results*

$\alpha$ -Amino acids, anthranilic acid, and *N*-phenylanthranilic acid responded negatively to both the tests. The negative results in case of  $\alpha$ -amino acids are understandable owing to their existence as zwitter-ions.

### *The nature of the product in the acriflavine/sodium nitrite test*

The violet colour observed is presumably due to the formation of the acriflavine diazonium ion, which, though not very stable, is fairly stable at room temperature. This presumption is based on the fact that (a) like other diazonium ions, acriflavine diazonium ion starts decomposing within a few minutes when kept at room temperature, and the colour starts fading; the decomposition proceeds more rapidly on heating the reaction mixture; the colour can be stabilized by keeping the reaction mixture in an ice-bath, and (b) the violet acriflavine diazonium ion couples with alkaline  $\beta$ -naphthol, giving a reddish-violet or brownish-violet dye (at  $<5^\circ$ ); the resultant dye dissolves in acetone, giving a deep red-coloured solution.

### *The nature of the product in the acriflavine/potassium chromate test*

Studies have indicated that the yellow to brownish-yellow precipitate which results on adding potassium chromate solution to a solution of acriflavine in acid medium, is due, most probably, to the formation of the chromate salt of acriflavine,  $[\text{C}_{14}\text{H}_{15}\text{N}_3\text{Cl}]_2\text{CrO}_4$ . It can be filtered and dried, and can be dissolved in hot water or in acetone. That the product is a simple chromate salt of acriflavine is confirmed by the fact that its solution again gives the usual tests for acriflavine; thus, for example, it gives a violet colour with nitrous acid, and the product will couple with alkaline  $\beta$ -naphthol, giving a reddish-violet dye (soluble in acetone to give a deep red colour). This experiment also indicates that both the amino groups remain intact in the product (acriflavine chromate); hence the formation of any oxidation product of acriflavine by the reaction with chromate can be ruled out. Tests for chloride are positive on the product from a Lassaigne sodium fusion test, but negative on an aqueous solution of the compound itself, showing that the chloride is very firmly bound. It can be stated that the product is probably the monohydrochloride of 2,8-diamino-10-methylacridinium chromate, in which chloride ion (attached to heterocyclic nitrogen) of acriflavine



has been replaced by the bivalent chromate ion (involving two molecules of the dye). We have also observed the instantaneous precipitation of a similar type of salt when a dilute neutral solution of acriflavine was treated with a neutral solution of potassium dichromate, potassium ferrocyanide, potassium ferricyanide, or sodium nitroprusside. The formation of analogous salts has been reported in the literature; these include *N*-methylacridinium chromate,<sup>8</sup> acridinium perchlorate,<sup>9</sup> and 2,8-diamino-10-methylacridinium antimonyl tartrate (acriflavine antimonyl tartrate).<sup>10</sup>

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**Summary**—The dye acriflavine is used for the selective detection of the carboxylic acid group in organic compounds. Two simple, rapid, and reliable colour tests are reported; these are based on the development of a violet colour and a yellow to yellowish-brown precipitate when a carboxylic acid is treated with acriflavine/sodium nitrite and acriflavine/potassium chromate respectively. Other acidic compounds such as phenols, thiophenols, sulphinic acids, sulphonamides, and acid imides do not interfere. Sulphonic acids (with the exception of their amino derivatives) interfere with both the tests. Enols and salts of organic bases do not interfere in the former test, whereas they do interfere in the latter test. The probable nature of the reaction products in both the tests has been discussed. Based on the former reaction, a procedure is described for the selective detection of nitrite ion. The limit of detection is 25  $\mu\text{g}$  of nitrite per ml. Only iodide interferes.

**Zusammenfassung**—Der Farbstoff acriflavin wird zum selektiven Nachweis der Carbonsäuregruppe in organischen Verbindungen verwendet. Es wird über zwei einfache, rasch auszuführende und zuverlässige Farbttests berichtet. Diese Tests beruhen auf der Entwicklung einer violetten Farbe und eines gelben bis gelblichbraunen Niederschlages, wenn eine Carbonsäure mit Acriflavin-Natriumnitrit bzw. Acriflavin-Kalium-chromat behandelt wird. Andere saure Verbindungen wie Phenole, Thiophenole, Sulfinsäuren, Sulfonamide und saure Imide stören nicht. Sulfonsäuren (außer ihren Aminoderivaten) stören beide Tests. Enole und Salze organischer Basen stören nicht im ersten, jedoch im zweiten Test. Die wahrscheinliche Natur der Reaktionsprodukte in beiden Tests wurde diskutiert. Auf Grund der ersten Reaktion wird ein Verfahren zum selektiven Nachweis des Nitritions beschrieben. Die Nachweisgrenze beträgt 25  $\mu\text{g}$  Nitrit pro ml. Nur Jodid stört.

**Résumé**—On utilise le colorant acriflavine pour la détection sélective du groupement acide carboxylique dans les composés organiques. On rapporte deux essais colorés simples, rapides et fidèles; ils sont basés sur le développement d'une coloration violette et d'un précipité jaune à brun-jaunâtre lorsqu'un acide carboxylique est traité à l'acriflavine/nitrite de sodium et à l'acriflavine/chromate de potassium respectivement. D'autres composés à caractère acide tels les phénols, thiophénols, acides sulfoniques, sulfamides et imides n'interfèrent pas. Les acides sulfoniques (à l'exception de leurs dérivés aminés) gênent dans les deux essais. Les énols et les sels de bases organiques ne gênent pas dans le premier essai, tandis qu'ils interfèrent dans le second. On discute de la nature probable des produits de la réaction dans les deux essais. On décrit une technique, basée sur la première réaction, pour une détection sélective de l'ion nitrite. La limite de détection est de 25  $\mu\text{g}$  de nitrite par ml. Seul l'iodure interfère.

## REFERENCES

1. F. Feigl, *Spot Tests in Organic Analysis*, 6th Ed. Elsevier, Amsterdam, 1960.
2. M. Gailliot, *Quart. J. Pharm. Pharmacol.*, 1934, **7**, 63.
3. H. Berry, *Pharm. J.*, 1941, **146**, 181.
4. H. W. van Urk, *Pharm. Weekblad*, 1928, **65**, 1227.
5. P. J. Udall, *Analyst*, 1932, **57**, 295.
6. W. H. C. Shaw and G. Wilkinson, *ibid.*, 1935, **77**, 127.
7. O. N. Yalcindag, *Pharm. Zentralhalle*, 1950, **89**, 186.
8. H. Decker and G. Dunant, *Ber.*, 1909, **42**, 1176.
9. K. A. Hofmann, A. Metzler, and K. Höbold, *Ber.*, 1910, **43**, 1080.
10. U. N. Brahmachari, *Indian J. Med. Res.*, 1923, **11**, 405.

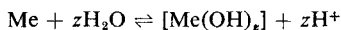
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## Zur Verbesserung der Reproduzierbarkeit der Meßwerte bei photometrischen Bestimmungsverfahren

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DIE MESSGENAUIGKEIT moderner Spektralphotometer liegt, wie Ackermann und Kaden<sup>1</sup> zeigen konnten, in den meisten Fällen weit über der Präzision der Meßwerte, die von sorgfältig vorbereiteten Analysenproben erhalten werden. Im allgemeinen werden bei der Probenvorbereitung auch Fehler durch Masse- und Volumenbestimmungen klein sein, so daß als wichtigste Fehlerquelle die farbige Substanz und deren Bildung angesehen werden muß. Hier kann man durch Auswahl geeigneter Reaktionsbedingungen meist noch eine Verbesserung erreichen.

Bei der photometrischen Bestimmung eines Metallions als Komplexverbindung können besonders bei hochgeladenen Ionen z.B., noch dadurch Komplikationen eintreten, daß bei Zugabe von Lauge zur pH-Einstellung an der Eintropfstelle infolge der hohen Hydroxidionenkonzentration je nach Metall und Komplexbildner Hydrolyse- und Polykondensationsreaktionen nach\*



ablaufen können. Da derartige Hydrolyseprodukte im allgemeinen kinetisch recht stabil sind, kann die Reaktion mit anderen Liganden beeinträchtigt und auf die Weise die Präzision des Analysenverfahrens vermindert werden. Wie wir bei der photometrischen Bestimmung von Niob(V) und Tantal (V) mit Dibromgallussäure zeigen konnten,<sup>2</sup> lassen sich die genannten unerwünschten Nebenreaktionen durch Zusatz von Hilfskomplexbildnern unterdrücken.

Als Beispiel soll hier das bekannte Verfahren zur Eisen(III)-Bestimmung mit Thiocyanat gebracht werden, das bekanntlich hinsichtlich der einzuhaltenden Reaktionsbedingungen ziemlich empfindlich ist. Für eine Eisen(III)-Lösung mit  $c = 1 \mu\text{g/ml}$  wurden bei verschiedenen pH-Werten folgende Variationskoeffizienten ermittelt:

|                    |     |     |     |
|--------------------|-----|-----|-----|
| $\frac{pH}{V, \%}$ | 1   | 3   | 4   |
|                    | 1.5 | 2.2 | 4.4 |

Wegen der mit dem pH steigenden Tendenz zur Bildung von Hydroxiverbindungen nimmt die Präzision der Meßwerte in der gleichen Richtung ab.

Berechnet man nach den Gesetzen der Fehlerfortpflanzung den Gesamtfehler ohne Berücksichtigung der Unregelmäßigkeiten beim Ablauf der Komplexbildung, so ergibt sich nach

$$\frac{\sigma_y}{y} = \sqrt{\left(\frac{\sigma_E}{E}\right)^2 + \sum_{i=1}^2 \left(\frac{\sigma V_i}{V_i}\right)^2}$$

für  $P = 68.3\%$  ein relativer Fehler von 0,2%. Der Gerätefehler ist dabei mit 0,1%, die Ungenauigkeiten bei den Volumenmessungen sind nach Eckschlager<sup>3</sup> angesetzt worden. Ein Vergleich des berechneten Wertes mit den in der Zusammenstellung enthaltenen Variationskoeffizienten der

\* Die Ladung der Teilchen blieb unberücksichtigt.

Versuchsreihen zeigt eindeutig, daß die—mehr oder weniger beeinflusste—Komplexbildung offensichtlich die Hauptfehlerquelle darstellt.

Führt man die Versuche bei pH 4 in Gegenwart verschiedener Hilfskomplexbildner durch, so erhält man bei:

|                                  |             |
|----------------------------------|-------------|
| ÄDTA ( $s = 0,1$ )               | $V = 1,2\%$ |
| Ammoniumoxalat<br>( $s = 0,1$ )  | $V = 2,4\%$ |
| Natriumchlorid<br>( $s = 10^4$ ) | $V = 2,5\%$ |

( $s =$  molares Verhältnis Hilfskomplexbildner zu Metallion)

Eine Überprüfung der Variationskoeffizienten mit dem  $F$ -Test ergab sowohl für die Paare pH 1 und pH 4 als auch in Anwesenheit verschiedener Komplexbildner signifikante Unterschiede. Die Struktur des gebildeten, offensichtlich ternären Chelats wird zur Zeit noch weiter untersucht. Die beobachtete Verbesserung der Präzision des Verfahrens ist aber eindeutig auf den Zusatz der Hilfskomplexbildner zurückzuführen. Zu ähnlichen Ergebnissen kommt man bei der Bestimmung von Titan(IV) mit Tiron bzw. Chromotropsäure, wie das aus Tabelle I zu entnehmen ist. Die mitgeteilten Versuche

TABELLE I.—EINFLUSS VON HILFSKOMPLEXBILDNERN AUF DIE PRÄZISION DER BESTIMMUNG VON TITAN MIT TIRON BZW. MIT CHROMOTROPSÄURE

| Hilfskomplexbildner<br>( $s = 1$ ) | Variationskoeffizient, % |                 |
|------------------------------------|--------------------------|-----------------|
|                                    | Tiron                    | Chromotropsäure |
| —                                  | 0,5                      | 0,7             |
| Ammoniumoxalat                     | 0,2                      | 0,6             |
| Ammoniumtartrat                    | 0,4                      | 0,5             |
| Natriumchlorid                     | 0,5                      | 0,7             |

zeigen zwar eindeutig, daß die Verwendung von Hilfskomplexbildnern die Präzision photometrischer Bestimmungsverfahren verbessern kann, lassen aber noch keinen Schluß über die Wirkungsweise und über die Art der einzusetzenden Liganden zu. Sicher spielt die Stabilität der einzelnen Komplexe eine ebenso wichtige Rolle wie kinetische Probleme. Bei der Auswahl der Hilfskomplexbildner, die vorerst noch auf empirischer Grundlage erfolgen muß, ist außerdem zu beachten, daß auch unter den veränderten Verhältnissen das Lambert-Beersche Gesetz möglichst gültig bleiben soll.

#### Experimentelles

Zur Vorbereitung der Proben wurden nacheinander 5 ml der Metall-Stammlösung, Hilfskomplexbildner und Reagenzien zusammengegeben, der pH-Wert eingestellt und auf 50 ml aufgefüllt. Die photometrischen Messungen erfolgten am Beckman-Spektralphotometer, Modell DU, gegen eine Blindprobe ( $d = 10$  mm).

Eisen(III) ( $1 \mu\text{g/ml}$ ) wurde bei  $480 \text{ nm}^4$ , und

Titan(IV) ( $1 \mu\text{g/ml}$  bzw.  $1,25 \mu\text{g/ml}$ ) mit Tiron<sup>4</sup> bei  $410 \text{ nm}$  oder mit Chromotropsäure<sup>5</sup> bei  $420 \text{ nm}$  untersucht.

Die Variationskoeffizienten sind mit  $f = 9$  Freiheitsgraden ermittelt worden, wobei angenommen wurde, daß Gauß-Verteilung vorliegt.

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**Zusammenfassung**—Die Zugabe eines schwachen Komplexbildners zu den für die spektralphotometrische Bestimmung vorbereiteten Problemlösungen kann die Reproduzierbarkeit der Meßwerte durch Kontrolle der Nebenreaktionen verbessern. Als Beispiel wurden die Bestimmungen von Eisen(III) mit Thiocyanat und von Titan(IV) mit Tiron oder mit Chromotropsäure untersucht.

**Summary**—The addition of a weak complexing agent to control interfering side-reactions is shown to increase the precision of the photometric determination of iron(III) with thiocyanate and of titanium(IV) with Tiron or with chromotropic acid.

**Résumé**—On montre que l'addition d'un agent complexant faible pour contrôler les réactions secondaires qui gênent accroît la précision du dosage photométrique du fer (III) par le thiocyanate et du titane(IV) par le Tiron ou l'acide chromotropique.

#### LITERATUR

1. G. Ackermann und W. Kaden, *Jenaer Rundschau.*, 1969, **14**, 168.
2. G. Ackermann und S. Koch, *Talanta*, 1970, **17**, 757.
3. K. Eckschlager, *Fehler bei chemischen Analysen*, S. 36. Akademische Verlagsgesellschaft Geest und Portig K. G., Leipzig, 1964.
4. O. G. Koch und G. A. Koch-Dedic, *Handbuch der Spurenanalyse* Springer, Berlin, 1964.
5. L. Sommer, *Acta Chim. Acad. Sci. Hung.*, 1959, **18**, 121.

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### Determination of arsenic and selenium in steel by an X-ray technique utilizing chemical preconcentration\*

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THE CHEMISTRY GROUP of Crucible Materials Research Center has always been confronted with the task of analysing traces and of employing prechemical concentration techniques when the sensitivity of direct X-ray, optical emission or atomic absorption methods is not adequate.

Elements such as tellurium, selenium, arsenic and antimony have been some of the subjects of such a task, as direct X-ray or optical emission methods of analysis for them are inadequate and chemical methods are lengthy and involved. The reduction of these elements to their elemental state by tin(II) chloride is reported by Schoeller.<sup>1</sup> Goto and Kakito<sup>2</sup> state that tin(II) chloride will quantitatively separate 0.01% tellurium from iron. Burke *et al.*<sup>3</sup> used tin(II) chloride to separate tellurium which was then collected on a micropore membrane.

The author<sup>4</sup> modified this approach to determine both tellurium and selenium in various steels in the presence of arsenic used as carrier for selenium. Burke and Yanak<sup>5</sup> have reported the use of sodium hypophosphite for the separation of arsenic in nickel and iron base alloys and Luke<sup>6</sup> used ammonia for the precipitation of 0–300  $\mu\text{g}$  of arsenic, with iron(III) as a carrier, from copper base alloys.

The use of arsenic as carrier was further investigated. During later experimental work it was found that both selenium and arsenic can be used as carriers for each other, with tin(II) chloride as the reductant, for the quantitative separation of elemental arsenic or selenium from iron matrices.

#### EXPERIMENTAL

##### *X-Ray apparatus*

A Siemens X-ray fluorescence spectrograph type "Crystalloflex IV" with an X-ray generator and control having a full-wave rectified power supply voltage and current regulation up to 50 kV and 40 mA in air, and a high purity gold target, was used.

##### *Materials*

*Arsenic solution*, 10  $\mu\text{g}/\text{ml}$ . Dissolve 1.00 g of arsenic metal in 10 ml of *aqua regia* and dilute to 1 litre. Dilute 10 ml of this solution a 100-fold to 10  $\mu\text{g}/\text{ml}$ .

*Selenium solution*, 10  $\mu\text{g}/\text{ml}$ . Dissolve 1.0 g of selenium metal in 10 ml of *aqua regia* and dilute to 1 l. Dilute 10 ml of this solution a 100-fold to 10  $\mu\text{g}/\text{ml}$ .

\* Presented at the 22nd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio U.S.A. March 1, 1971. Paper No. 40.

*Tin(II) chloride solution*, 1.0 g/ml. Dissolve 100 g of tin(II) chloride in 40 ml of concentrated hydrochloric acid and dilute to 100 ml with concentrated hydrochloric acid.

#### Procedure

Dissolve 0.1–1 g of sample in 40 ml of hydrochloric acid: nitric acid mixture (7:1). Evaporate the solution to approximately 25 ml and add 300  $\mu\text{g}$  of arsenic if selenium is to be determined or 300  $\mu\text{g}$  of selenium if arsenic is to be determined. (If both elements are to be determined use two separate samples.)

Dilute to approximately 40 ml and add with stirring 10 ml of tin(II) chloride solution. Filter off after 10 min on a micropore membrane\* (SMWP 04700-25 each  $5\mu\text{m}$  white plain, 47 mm), wash the precipitate with 3M hydrochloric acid and water, air-dry for 1 min and mount the membrane in a solution sample holder consisting of a plastic body pressed against a frame of aluminium by a threaded ring. The use of the solution holder described was adopted as it was found convenient and reproducible, allowing exposure of the whole circular area covered by the sample, and non-destructive to the membrane, which can be removed, stored and mounted again.

Place the mounted membrane in the X-ray spectrograph and determine arsenic or selenium according to the following conditions:

|                                     |                                     |
|-------------------------------------|-------------------------------------|
| Primary voltage                     | 50 kV                               |
| Primary current                     | 40 mA                               |
| Detector scintillator               |                                     |
| Detector voltage                    | 500–600 V                           |
| Pulse-height analyser baseline      | 8 V                                 |
| Pulse-height analyser channel width | 8 V                                 |
| Preset time                         | 60 sec                              |
| Crystal—lithium fluoride            | 1st order $K\alpha$ radiation       |
| $2\theta$ values                    | arsenic 34.03°      selenium 31.89° |

Measure the counts accumulated during a fixed time, also the number of counts accumulated at one degree above the  $2\theta$  value; take the difference between the two counts for the element sought and divide it by the fixed time to calculate the number of counts rate.

Plot counts per second against  $\mu\text{g}$  of arsenic or selenium to construct calibration graphs, using a set of five synthetic standards consisting of 1.0 g of pure iron containing 0–200  $\mu\text{g}$  of the element of interest, and treated according to the procedure.

## RESULTS AND DISCUSSION

The calibration curves are both linear from 0 to 200  $\mu\text{g}$  but the arsenic curve intersects the origin whereas the selenium curve intersects the Y axis at 115 c/s (in our experiments). The high selenium blank is obtained at the selenium  $K\alpha$  peak during all selenium analyses (solids, pellets and residues and was attributed to either gold ( $L$  line) interference (gold target, air-path) or selenium impurities present in the gold target.

TABLE I.—ROLE OF AS AS CARRIER FOR Se

| Se added,<br>$\mu\text{g}$ | As added,<br>$\mu\text{g}$ | Se $K\alpha$ ,<br>cps |
|----------------------------|----------------------------|-----------------------|
| 0                          | 0                          | 113                   |
| 50                         | 0                          | 110                   |
| 50                         | 300                        | 268                   |
| 100                        | 50                         | 184                   |
| 100                        | 300                        | 422                   |
| 200                        | 100                        | 679                   |
| 200                        | 300                        | 700                   |
| 500                        | 300                        | 1500                  |
| 500                        | 400                        | 1560                  |

\* The membranes used were obtained from the Millipore Corporation of Bedford, Massachusetts, U.S.A. Three sizes of micropore membranes (0.22, 1.5 and  $5\mu\text{m}$ ) were evaluated. According to our findings no significant differences were noted in triplicate samples filtered through the three membranes. The  $5\text{-}\mu\text{m}$  membranes were adopted as the fastest and equally reliable for routine arsenic and selenium analyses.

The ability of arsenic and selenium to act as carriers for each other was confirmed experimentally (Tables I and II). One-gram samples of iron were used as matrix, the desired amounts of arsenic and selenium were added and subsequently all samples were processed as described in the procedure.

The results in Table I show the influence of the selenium precipitation with arsenic. The precipitation appears negligible when arsenic is absent, becomes rather uniform for equal levels of selenium when 100–300  $\mu\text{g}$  of arsenic are present and levels off when 300–400  $\mu\text{g}$  of arsenic are added. Therefore 300  $\mu\text{g}$  of arsenic was adopted as an adequate amount for the precipitation of

TABLE II.—ROLE OF Se AS CARRIER FOR As

| As added,<br>$\mu\text{g}$ | Se added,<br>$\mu\text{g}$ | As $K\alpha$ ,<br><i>cps</i> |
|----------------------------|----------------------------|------------------------------|
| 0                          | 0                          | 4                            |
| 50                         | 0                          | 4                            |
| 50                         | 100                        | 5                            |
| 50                         | 300                        | 148                          |
| 100                        | 200                        | 47                           |
| 100                        | 300                        | 255                          |
| 200                        | 300                        | 496                          |
| 250                        | 300                        | 507                          |
| 300                        | 400                        | 593                          |

10–200  $\mu\text{g}$  of selenium. The latter was satisfactorily determined by this method in amounts as high as 500  $\mu\text{g}$ , as the selenium calibration graph remains linear up to that level. For practical reasons, however, it is recommended that the amount of selenium recovered should be in the 10–200  $\mu\text{g}$  range.

The results given in Table II show the influence of selenium on the arsenic recovery. The precipitation of arsenic is negligible until 200  $\mu\text{g}$  of selenium are added, but still not complete until 300  $\mu\text{g}$  of selenium are present, so 300  $\mu\text{g}$  of selenium were used for the quantitative precipitation of 10–200  $\mu\text{g}$  of arsenic. When larger amounts of arsenic (250–300  $\mu\text{g}$ ) were present recoveries were incomplete. Increasing the amount of carrier (to 400  $\mu\text{g}$  of selenium) produced no significant improvement.

The results given in Tables III and IV show recoveries of both elements from synthetic samples, certified National Bureau Standards and Company standards. They represent results from low-alloy steels, stainless steel and iron matrices in general. The X-ray and chemical results given in

TABLE III.—DETERMINATION OF ARSENIC

| Sample           | Weight,<br>$\text{g}$ | As assumed,<br>$\mu\text{g}$ | As found,<br>$\mu\text{g}$ |
|------------------|-----------------------|------------------------------|----------------------------|
| NBS 55E          | 1.0                   | 60–80*                       | 80                         |
| NBS 9E           | 1.0                   | 80–90*                       | 70                         |
| NBS 10E          | 1.0                   | 40–60*                       | 70                         |
| 9402 Low Alloy   | 0.5                   | 90†                          | 80                         |
| 9403 Low Alloy   | 0.5                   | 70†                          | 65                         |
| 9404 Low Alloy   | 0.5                   | 90†                          | 81                         |
| 9405 Low Alloy   | 0.5                   | 80†                          | 76                         |
| 9406 Low Alloy   | 0.5                   | 40†                          | 38                         |
| A-18-8 Stainless | 1.0                   | 30†                          | 33                         |
| B-18-8 Stainless | 1.0                   | 100†                         | 103                        |

\* Certified value.

† Chemical value.

Table III for arsenic summarize the agreement between the two methods. In general the agreement is very good. Owing to lack of a reliable low selenium standard, NBS 339 (17 Cr–9 Ni) with a reported value of 0.247% selenium, was used (Table IV). A 0.15-g sample of NBS 339 was analysed and the amount of selenium found agreed very well with the certified value. Because of lack of any chemical methods for low selenium concentrations most of the selenium results in Table IV were obtained from synthetic samples.

TABLE IV.—DETERMINATION OF SELENIUM

| Sample           | Weight,<br>g | Se assumed,<br>$\mu\text{g}$ | Se found,<br>$\mu\text{g}$ |
|------------------|--------------|------------------------------|----------------------------|
| NBS 339          | 0.15         | 375*                         | 382                        |
| Low alloy 1      | 1.00         | 10†                          | 9                          |
| Low alloy 2      | 1.00         | 20†                          | 20                         |
| Low alloy 3      | 1.00         | 30†                          | 30                         |
| Low alloy 4      | 1.00         | 50†                          | 54                         |
| Low alloy 5      | 1.00         | 75†                          | 70                         |
| Low alloy 6      | 1.00         | 100†                         | 106                        |
| Low alloy 7      | 1.00         | 500†                         | 505                        |
| 8 18-8 Stainless | 0.50         | 200†                         | 200                        |
| 9 18-8 Stainless | 0.10         | 600†                         | 770                        |

\* Certified.

† Amount added.

The method is not recommended for either element above the 0.01% level, as more rapid and direct X-ray methods could be used if adequate standards were available. It could be useful for standardization and calibration even at levels as high as 0.2%, as it is as accurate as chemical methods and considerably faster. For amounts less than 0.001% larger samples could be used.

After the dissolution of the sample, if large amounts of silica and graphitic carbon are present, they should be filtered off before reduction with tin(II), as they may slow down the final filtration through the millipore membrane.

Significant amounts of arsenic are lost if the hydrochloric acid is added first, as arsenic(III) can then be either reduced to volatile arsine or escape as arsenic trichloride. The presence of nitric acid oxidizes arsenic to the quinquevalent state and thus prevents its loss. No interference attributed to nitric acid was encountered with either arsenic or selenium.

Antimony was also investigated as a possible element to be determined by this method. Selenium, arsenic and tellurium were used in various amounts (0–500  $\mu\text{g}$ ) as carriers and tin(II) chloride was used as the reductant. There was no indication of antimony being precipitated when present in amounts from 10 to 200  $\mu\text{g}$ . No interference from up to 200  $\mu\text{g}$  of tellurium was encountered with either arsenic or selenium. Tellurium can be determined by the same procedure without the need for a carrier.

#### Reproducibility

The standard deviations and coefficient of variation for 0.0078% arsenic and 0.24% selenium were 0.00035 and  $\pm 4.59\%$  for arsenic and 0.0105 and  $\pm 4.35\%$  for selenium (10 variates for arsenic and 5 for selenium).

#### Conclusions

It is apparent from the experimental results that co-precipitation of arsenic and selenium as the free metals by tin(II) can be achieved quantitatively at microgram levels (0–200  $\mu\text{g}$ ) of either element, provided that the element used as carrier is present at a suitable level.

Synthetic standards must be used to construct the working curves, which can be used successfully for a reasonable length of time.

Since 1967 this method has been used at the Crucible Materials Research Center for the determination of microgram amounts of both arsenic and selenium.

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**Summary**—A chemical X-ray method is proposed for determining trace amounts of arsenic and selenium in steel. The method utilizes a prechemical separation from the iron matrix and concentration of arsenic and selenium on a micropore membrane by reduction to the free metal by tin(II). Selenium was found to be a suitable carrier for arsenic (300  $\mu\text{g}$  of selenium for the quantitative precipitation of

10–200  $\mu\text{g}$  of arsenic). Arsenic (300  $\mu\text{g}$ ) was found to be a suitable carrier for up to 200  $\mu\text{g}$  of selenium. Up to 200  $\mu\text{g}$  of tellurium and antimony were experimentally found not to be co-precipitated with either arsenic or selenium.

**Zusammenfassung**—Eine chemische Röntgenmethode zur Bestimmung von Spuren Mengen Arsen und Selen in Stahl wird vorgeschlagen. Das Verfahren benutzt vorab eine chemische Abtrennung aus dem Grundmetall Eisen und Anreicherung von Arsen und Selen auf einer Micropore-Membran durch Reduktion mittels Zinn(II) zum freien Metall. Selen erwies sich als geeigneter Träger für Arsen (300  $\mu\text{g}$  Selen zur quantitativen Fällung von 10–200  $\mu\text{g}$  Arsen). Arsen (300  $\mu\text{g}$ ) erwies sich als geeigneter Träger für bis zu 200  $\mu\text{g}$  Selen. Es zeigte sich, daß bis zu 200  $\mu\text{g}$  Tellur und Antimon nicht mit Arsen oder Selen mitgefällt werden.

**Résumé**—On propose une méthode aux rayons X chimique pour la détermination de traces d'arsenic et de sélénium dans l'acier. La méthode utilise une séparation préchimique de la matrice de fer et la concentration de l'arsenic et du sélénium sur une membrane micropore par réduction en métal libre à l'étain(II). On a trouvé que le sélénium est un entraîneur convenable pour l'arsenic (300  $\mu\text{g}$  de sélénium pour la précipitation quantitative de 10–200  $\mu\text{g}$  d'arsenic). On a trouvé que l'arsenic (300  $\mu\text{g}$ ) est un entraîneur convenable du sélénium jusqu'à 200  $\mu\text{g}$ . On a trouvé expérimentalement que jusqu'à 200  $\mu\text{g}$  de tellure et d'antimoine ne sont pas coprecipités avec l'arsenic ou le sélénium.

#### REFERENCES

1. W. R. Schoeller, *Analyst*, 1939, **64**, 318.
2. H. Goto and Y. Kakito, *Bunseki Kagaku* 1954, **3**, 299.
3. E. K. Burke, M. Yanak and C. H. Albright, *Anal. Chem.*, 1967, **39**, 14.
4. J. P. McKaveney, H. E. Baldwin and G. L. Vassilaros, *J. Metals*, 1968, **54**.
5. E. K. Burke and M. Yanak, *Anal. Chem.* 1969, **41**, 863.
6. C. L. Luke, *Anal. Chim. Acta* 1968, **41**, 237.

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### Potassium thiocarbonate as a precipitant for platinum metals

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THE USE of potassium thiocarbonate (PTC) instead of gaseous hydrogen sulphide in qualitative<sup>1–3</sup> and quantitative<sup>4–6</sup> analysis has been extensively studied. The present communication gives gravimetric procedures for milligram quantities of ruthenium(III), rhodium(III), palladium(II) or platinum(IV), in acidic medium. The sulphides of ruthenium(III),<sup>7</sup> rhodium(III),<sup>8</sup> palladium(II) and platinum(IV)<sup>9</sup> are usually precipitated by passing hydrogen sulphide into a hot hydrochloric acid solution of the metal ion, but the precipitation is slow and incomplete, particularly in the case of ruthenium. According to Beamish<sup>10</sup> the sulphide method for ruthenium is not good under any circumstances. However, ignition of the sulphides (except ruthenium) to the oxides and subsequent reduction in a current of hydrogen to the metals has proved very satisfactory, particularly in the case of rhodium and platinum. The various reagents used for the determination of these metals have been reviewed by Beamish.<sup>10–12</sup> The method recommended by Taimni and Salaria<sup>13</sup> for the determination of platinum metals is based on the addition of a large excess of sodium sulphide to a slightly ammoniacal solution of the chlorides of these metals, followed by the addition of acetic acid and ammonium acetate, thus yielding the sulphides of these metals for direct weighing. This method has been examined critically by Sant *et al.*<sup>14</sup> who concluded that the method is not as satisfactory and accurate as claimed. On the other hand, potassium thiocarbonate causes a speedy,



clean and complete precipitation of these metals from hot acid solution, without need for the pressure system required with hydrogen sulphide in the case of ruthenium.<sup>15</sup> The sulphides are then ignited in a current of hydrogen and converted into the metals, which are weighed. The results confirm that the method is efficient, convenient and economical.

### EXPERIMENTAL

#### Reagents

*Platinum metal solutions.* Standard solutions of ruthenium and rhodium were prepared by dissolving ruthenium(III) and rhodium(III) chlorides in dilute hydrochloric acid, and standardizing by hydrolytic precipitation methods.<sup>16</sup> The palladium solution was made by dissolving palladium(II) chloride in dilute hydrochloric acid and standardizing by the dimethylglyoxime method. Platinum solution was prepared by dissolving chloroplatinic acid in distilled water and standardizing by precipitation of the metal with formic acid.

*Diverse ion solutions.* Prepared by dissolving known amounts of analytical-grade reagents in distilled water or, if necessary in dilute hydrochloric acid.

*Potassium thiocarbonate stock reagent, 1M.* Prepared as reported earlier<sup>17-20</sup> and fresh dilutions were used as required.

TABLE I.—SEPARATION OF RUTHENIUM, RHODIUM, PALLADIUM AND PLATINUM FROM DIVERSE IONS

| Ruthenium (44.90 mg taken) |              | Rhodium (25.80 mg taken) |              |
|----------------------------|--------------|--------------------------|--------------|
| Foreign ion added, mg      | Ru found, mg | Foreign ion added, mg    | Rh found, mg |
| Ni, 35                     | 44.60        | Ni, 30                   | 25.90        |
| Zn, 45                     | 44.60        | Zn, 35                   | 25.80        |
| Mn(II), 40                 | 44.80        | Mn(II), 20               | 25.70        |
| Al, 50                     | 44.60        | Al, 40                   | 25.80        |
| Fe(III), 30                | 44.70        | Fe(III), 35              | 25.70        |
| Ti, 30                     | 44.80        | Ti, 24                   | 25.70        |
| Zr, 30                     | 44.70        | Zr, 25                   | 25.90        |
| Th, 20                     | 44.60        | Th, 16                   | 25.90        |
| Palladium (23.52 mg taken) |              | Platinum (23.7 mg taken) |              |
| Foreign ion added, mg      | Pd found, mg | Foreign ion added, mg    | Pt found mg  |
| Ni, 30                     | 23.36        | Ni, 20                   | 23.60        |
| Zn, 30                     | 23.40        | Zn, 30                   | 23.70        |
| Mn(II), 35                 | 23.45        | Cu(II), 40               | 23.50        |
| Al, 40                     | 23.42        | Ag, 30                   | 23.70        |
| Fe(III), 30                | 23.45        | Au, 30                   | 23.60        |
| Ti, 40                     | 23.40        | Ca, 40                   | 23.80        |
| Zr, 30                     | 23.50        | Sr, 30                   | 23.60        |
| Th, 15                     | 23.60        | Ba, 50                   | 23.80        |
|                            |              | Mg, 35                   | 23.60        |
|                            |              | Ti, 25                   | 23.60        |
|                            |              | Zr, 15                   | 23.50        |
|                            |              | Th, 20                   | 23.50        |

### Procedure

An aliquot of platinum metal solution, containing 0.2 mg of the metal per ml, was adjusted to pH 0.5–0.7 (yellowish-green spot on Methyl Violet paper). The solution was heated to boiling and 0.5M PTC added dropwise with constant stirring till no more precipitate formed. The precipitate was digested over a steam-bath for 15–20 min. After cooling, the precipitate was filtered off on a Whatman No. 42 paper and washed with hot water till the washings were free from potassium ions. After drying, the filter paper was charred over a low flame in a tared weighed Rose crucible. The product was reduced to the metal in an atmosphere of hydrogen and finally cooled in a nitrogen atmosphere. In the case of platinum the reduction with hydrogen gas was not necessary and the precipitate was ignited in air.

### Separation and determination of Ru(III), Rh(III), Pd(II) or Pt(IV) in admixture with foreign ions

Ruthenium or rhodium or palladium was determined by the procedure given, in a mixture with a known amount of Al, Fe(III), Ni, Zn, Mn(II), Ti, Zr or Th. The foreign ions remained in solution. Platinum was determined in binary mixtures with Cu(II), Ag, Au(III), Ni, Zn, Ca, Sr, Ba, Mg, Ti, Zr or Th. Copper was precipitated from cold acidic solution (pH 0.7–1.0), platinum remaining in solution and being precipitated from the filtrate as described above. Silver was precipitated with PTC from ammoniacal solution while platinum(IV) remained in solution, being precipitated from the filtrate by the addition of hydrochloric acid and boiling. Gold(III) was separated from a binary mixture with Pt(IV) by reducing it to the metal with oxalic acid, and the platinum precipitated from the filtrate with PTC. Nickel remained in solution in aqueous medium. Platinum(IV) was separated from Ca, Sr, Ba, Mg, Ti, Zr or Th by adding excess of PTC followed by a large excess of 6M hydrochloric acid, heating to boiling to decompose the thiosalt of platinum(IV) completely, and then letting cool to room temperature. The precipitate of  $\text{PtS}_2$  was filtered off, washed with water and ignited to the metal.

### RESULTS

Analysis of binary mixtures of ruthenium(III), rhodium(III), palladium(II) or platinum(IV) with one of the foreign cations mentioned, gave the results shown in Table I, the largest relative error being 0.7% and the average relative error 0.2%.

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**Summary**—Potassium thiocarbonate reagent is proposed for the gravimetric determination of ruthenium(III), rhodium(III), palladium(II) and platinum(IV) in a highly acidic medium (pH 0.5–0.7) under suitable conditions. Ni, Zn, Mn(II), Al, Fe(III), Ti(IV), Zr, Th, Ca, Ba, Sr and Mg do not interfere. The largest relative error is 0.7% and the average error 0.2%.

**Zusammenfassung**—Kaliumthiocarbonat wird als Reagens zur gravimetrischen Bestimmung von Ruthenium(III), Rhodium(III), Palladium(II) und Platin(IV) in stark saurem Medium (pH 0,5–0,7) unter geeigneten Bedingungen vorgeschlagen. Ni, Zn, Mn(II), Al, Fe(III), Ti(IV), Zr, Th, Ca, Ba, Sr und Mg stören nicht. Der größte relative Fehler beträgt 0,7%, der durchschnittliche Fehler 0,2%.

**Résumé**—On propose le thiocarbonate de potassium comme réactif pour le dosage gravimétrique des ruthénium(III), rhodium(III), palladium(II) et platine(IV) en milieu fortement acide (pH 0,5–0,7) dans des conditions convenables. Ni, Zn, Mn(II), Al, Fe(III), Ti(IV), Zr, Th, Ca, Ba, Sr et Mg n'interfèrent pas. L'erreur relative la plus grande est 0,7% et l'erreur moyenne 0,2%.

### REFERENCES

1. K. N. Johri, *Indian J. Appl. Chem.*, 1963, **26**, 114.
2. *Idem*, *Chemical Analysis Without H<sub>2</sub>S, Using Potassium Trithiocarbonate*, 2nd Ed. Asia Publishing House, Bombay, 1968.

3. K. N. Johri and K. Singh, *Curr. Sci.*, 1965, **34**, 78.
4. *Idem*, *Indian J. Appl. Chem.*, 1965, **28**, 90.
5. *Idem*, *Bull. Chem. Soc. Japan*, 1967, **40**, 990.
6. K. N. Johri, K. Singh and N. K. Kaushik, *Talanta*, 1969, **16**, 432.
7. W. W. Scott, *Standard Methods of Chemical Analysis*, Vol. I, p. 746. Van Nostrand, New York, 1946.
8. W. J. Allan and F. E. Beamish, *Anal. Chem.*, 1950, **22**, 451.
9. D. S. Jackson and F. E. Beamish, *ibid.*, 1950, **22**, 813.
10. F. E. Beamish, *Analytical Chemistry of Noble Metals*, p. 254. Pergamon, London, 1966.
11. *Idem*, *Talanta*, 1958, **1**, 3.
12. *Idem*, *ibid.*, 1966, **13**, 773.
13. I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 1954, **11**, 329.
14. S. B. Sant, A. Chow and F. E. Beamish, *Anal. Chem.*, 1961, **33**, 1257.
15. M. N. Rao, *Z. Anal. Chem.*, 1967, **227**, 326.
16. F. E. Beamish, *Analytical Chemistry of Noble Metals*, pp. 253, 271. Pergamon, London, 1966.
17. K. N. Johri and K. Singh, *Indian J. Chem.*, 1965, **3**, 158.
18. *Idem*, *Analyst*, 1965, **90**, 745.
19. K. N. Johri and N. K. Kaushik, *ibid.*, 1968, **93**, 792.
20. *Idem*, *Indian J. Chem.*, 1969, **7**, 517.

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### Amperometric complex-formation titration of traces of thorium

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IN A PREVIOUS COMMUNICATION<sup>1</sup> it was shown that the range of amperometric complex-formation titrations of metal ions with indication of the end-point by following the anodic wave of the excess of ligand as proposed by Campbell and Reilley<sup>2</sup> could be extended to the 1- $\mu$ g level by using the more sensitive rotating mercury electrode instead of the dropping mercury electrode. Assuming that the reaction proceeds rapidly, the condition

$$K_M'c_M \geq 2 \times 10^3$$

was derived for a sharp end-point, where  $K_M'$  is the conditional stability constant and  $c_M$  is the original concentration of the metal ion. Results of titrations of copper<sup>1</sup> and the alkaline earths<sup>3</sup> were reported. In the present paper the determination of thorium with EDTA as chelating agent is described.

From the values of  $\log K_M'$  tabulated in Ringbom's monograph,<sup>4</sup> it follows that even at a pH value of 2.0 a sharp end-point in the titration of thorium at the  $\mu$ M concentration level may be expected. A low pH is favourable because most of the other elements will have very low values of  $\log K'$ , lowering the interference to be expected from their presence. Another advantage is that the necessary buffering of the solution can be done by the addition of dilute nitric acid, which does not interfere with the indication reaction by complexing with mercury as most of the common buffer components do.

As the limit for a sharp titration at the  $\mu$ M concentration level is reached at pH 2 another metal ion N complexing with EDTA can only be tolerated if  $\alpha_{L(N)} = 1 + K_N'c_N$  is about unity, as can be inferred from the theoretical considerations given in our first communication.<sup>1</sup> As the titrations are performed in a cell constructed for determinations in a volume of 10 ml, the minimum amount of thorium that can be determined is about 10 nmole, corresponding to about 2  $\mu$ g.

### EXPERIMENTAL

#### *Apparatus*

The apparatus used and the handling of the mercury electrode were described earlier.<sup>1,3</sup>

#### *Reagents*

All reagents used were of *pro analysi* quality. Dilutions were made with demineralized water.

### Procedure

The sample, containing about 2  $\mu\text{g}$  of thorium, is dissolved in 10 ml of a solution containing 0.1M potassium nitrate as supporting electrolyte and buffered to pH 2 with dilute nitric acid, and then titrated with  $10^{-4}\text{M}$  EDTA added from a 0.5-ml syringe burette. The diffusion current is measured polarographically at 0.32 V vs. S.C.E.

### RESULTS

Table I gives the results of a series of determinations of 2.2  $\mu\text{g}$  of thorium in 10 ml of solution in the presence of other ions.

TABLE I.—TITRATION OF 1  $\mu\text{M}$  THORIUM WITH  $10^{-4}\text{M}$  EDTA

| Amount of other ions      | Anion           | Error, % | Relative std. devn., % | No. of detns. |
|---------------------------|-----------------|----------|------------------------|---------------|
| —                         | $\text{NO}_3^-$ | 0.0      | 0.5                    | 4             |
| Fe(III) 0.6 $\mu\text{g}$ | $\text{NO}_3^-$ | +1.3     | 0.7                    | 4             |
| Ce(III) 150 $\mu\text{g}$ | $\text{NO}_3^-$ | -0.1     | 1.3                    | 3             |
| $\text{UO}_2$ 30 mg       | $\text{NO}_3^-$ | -1.9     | 0.5                    | 4             |
| Mg 2 mg                   | $\text{NO}_3^-$ | -0.8     | 2.1                    | 4             |
| Pb 20 $\mu\text{g}$       | $\text{NO}_3^-$ | -1.0     | 0.3                    | 4             |
| Bi 2 $\mu\text{g}$        | $\text{NO}_3^-$ | —        | —                      | 1*            |
| $\text{SO}_4$ 1 mg        | —               | +2.3     | 2.5                    | 3             |

\* The sum of Th + Bi was titrated.

### Comments on Table I

Iron(III) is expected to interfere because of its large conditional stability constant. However, as the rate of reaction between iron(III) and EDTA at pH 2 is very small at low concentrations, about 1  $\mu\text{g}$  of iron(III) can be present without interference.

Amounts of lead larger than 20  $\mu\text{g}$  interfere because of the relatively large values of the conditional stability constant of the lead-EDTA complex.

As sulphate forms complexes with thorium, large amounts of this ion should be avoided. The 1 mg mentioned in the Table has to be considered as the maximum amount that can be tolerated under the experimental conditions.

According to Maxwell and Graham<sup>5</sup> Th can be separated from most of the other metals by electrolysis at a mercury pool electrode. In combination with this electrolytic separation the method becomes very selective for thorium. The results given in Table II were obtained after electrolysis of the solution with a mercury pool electrode placed in a magnetic field as proposed by Center *et al.*<sup>6</sup> The time needed for this separation was 30 min; the time for a titration is only a few minutes.

TABLE II.—TITRATION OF 1  $\mu\text{M}$  THORIUM WITH  $10^{-4}\text{M}$  EDTA FOLLOWING ELECTROLYSIS WITH A MERCURY POOL ELECTRODE

| Amount of metal added before electrolysis | Anion            | Error % | Relative std. devn., % | No. of detns. |
|---|------------------|---------|------------------------|---------------|
|   | $\text{NO}_3^-$  | —       | 0.5                    | 3             |
| Pb 2 mg                                   | acetate          | -2.6    | 0.1                    | 3             |
| Cu 1 mg                                   | $\text{ClO}_4^-$ | +0.2    | 0.8                    | 3             |
| Ag 1 mg                                   | $\text{NO}_3^-$  | -0.3    | 0.4                    | 3             |
| Bi 200 $\mu\text{g}$                      | $\text{NO}_3^-$  | +3.6    | 0.1                    | 3             |
| Fe(III) 60 $\mu\text{g}$                  | $\text{ClO}_4^-$ | -0.1    | 0.9                    | 3             |
| Fe(III) 300 $\mu\text{g}$                 | $\text{ClO}_4^-$ | 10      | —                      | 1             |

### DISCUSSION

The time needed for a titration is only a few minutes. In view of the high conditional constant of thorium compared to the elements left in solution after electrolysis with a mercury pool electrode

the reported method is very selective for  $\mu\text{g}$  amounts of thorium in the presence of relatively large amounts of other ions, as was demonstrated for a few representative metals. We do not expect other metals to interfere.

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**Summary**—Thorium has been determined in the microgram range by complexometric titration with EDTA. The end-point was detected by following the anodic wave of EDTA at a rotating mercury electrode. It has been shown that thorium can be titrated in the presence of large amounts of other metals. Following electrolysis at a mercury pool electrode the titration is selective for thorium.

**Zusammenfassung**—Thorium wurde im Mikrogrammbereich durch komplexometrische Titration mit EDTA bestimmt. Der Endpunkt wurde durch Messung der anodischen Stufe von EDTA an einer rotierenden Quecksilberelektrode ermittelt. Es wurde gezeigt, daß Thorium in Gegenwart großer Mengen anderer Metalle titriert werden kann. Nach einer Elektrolyse an einer massiven Quecksilberelektrode ist die Titration für Thorium selektiv.

**Résumé**—On a dosé le thorium dans le domaine du microgramme par titrage complexométrique à l'EDTA. Le point de fin de dosage est détecté en suivant la vague anodique de l'EDTA sur une électrode à mercure tournante. On a montré que l'on peut titrer le thorium en la présence de grandes quantités d'autres métaux. En suivant l'électrolyse sur une électrode de masse de mercure, le titrage est sélectif pour le thorium.

#### REFERENCES

1. F. Freese, H. J. Jasper and G. den Boef, *Talanta*, 1970, **17**, 945.
2. R. F. Campbell and C. M. Reilley, *ibid.*, 1962, **9**, 153.
3. G. den Boef, F. Freese, M. M. P. F. Kramer and H. Poppe, *ibid.*, 1970, **17**, 1006.
4. A. Ringbom, *Complexation of Metals in Analytical Chemistry*, Interscience, New York, 1963.
5. J. A. Maxwell and R. P. Graham, *Chem. Revs.*, 1950, **46**, 471.
6. E. J. Center, R. C. Overbeek and D. L. Chase, *Anal. Chem.*, 1951, **23**, 1134.

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### Determination of boron and nitrogen in boron nitride\*

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AS TECHNOLOGY has expanded, the need for high temperature materials has increased. One of the promising candidates for use at high temperature is boron nitride (BN). This compound is a white solid, inert to most reagents, resistant to oxidation, and with a high ( $>2000^\circ$ ) boiling point.<sup>1</sup> Chemically produced boron nitride powder can be pressed into shapes and fused with a small amount of binder (*e.g.* boric oxide). The compound can also be chemically vapour-deposited in a pure form. New methods of production have yielded high-purity BN; complete recovery of the two major elements is difficult, but necessary for precise analytical work. This paper describes improvements made in the methods for determining boron and nitrogen in any solid BN, pure or impure.

Boron has been determined in a variety of materials by converting it into boric acid, separating the impurities, and titrating the boric acid with sodium hydroxide after the addition of glycerol or mannitol. Lyutaya *et al.*<sup>2</sup> fused boron-containing refractory compounds (carbides, silicides, and nitrides) with barium carbonate or calcium oxide, and leached the melts with mineral acids. Boron

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nitride has been dissolved by fusing the sample in a platinum crucible with a mixture of sodium carbonate and sodium nitrate<sup>3,4</sup> and dissolving the melt with hydrochloric acid. Incomplete fusion, contamination from the platinum crucible, formation of cyanates or other nitrogen compounds with resulting poor precision were experienced when using this procedure on pure (>99% BN) boron nitride.

Boron nitride is so stable at high temperatures that the conventional Dumas method for nitrogen cannot be used; a modification was found<sup>5</sup> to give too large an error. A Kjeldahl procedure, as modified for nitrates, has been used successfully on poor quality BN but cannot be used on pure BN because the latter is insoluble in the reagents. Ormont and Samoilov<sup>6</sup> determined nitrogen in BN by heating it with potassium hydroxide in an iron vessel at 400–450° in a stream of hydrogen; the ammonia evolved was absorbed in excess of hydrochloric acid. Shafran and Levinson<sup>7</sup> fused BN with sodium hydroxide in a glass test-tube and absorbed the evolved ammonia in standard acid. Khartonova<sup>8</sup> sintered BN in a mixture of 2 parts sodium hydroxide to 1 part calcium oxide and swept out the ammonia gas with argon. A caustic fusion technique has been reported for the determination of small amounts of nitrogen in metal,<sup>9</sup> and was later modified by Kriege.<sup>4</sup> These procedures did not give good precision in the analysis of high purity BN; moreover, the apparatus was destroyed after one determination. Further modification of the Kriege procedure during the present investigation provided good precision for nitrogen in pure BN.

## EXPERIMENTAL

### Procedures

**Boron.** Weigh a 100-mg powdered sample into a 70-ml platinum crucible. Weigh out 3 g of sodium carbonate, mix about 2/3 of it with the sample, and place the remainder on top of the sample mixture. Put the lid on the crucible and heat in a muffle furnace at  $900 \pm 10^\circ$  for 20 min. Cool, then transfer the contents of the crucible into a 250-ml beaker with about 150 ml of water, carefully rinsing the crucible and lid. Add a few drops of Methyl Red indicator and concentrated hydrochloric acid to make the solution strongly acid. Cover the beaker and boil the contents gently until the carbon dioxide is removed. Cool and add sodium hydroxide solution dropwise until the solution is slightly basic, then just acidify with dilute hydrochloric acid. Titrate potentiometrically, using a recording titrator, with 0.1*N* sodium hydroxide (CO<sub>2</sub>-free) to the first equivalence point on the recorder chart. Add ~5 g of mannitol, dissolve it and titrate to the equivalence point.

**Nitrogen.** Weigh a 100-mg ground and sieved (<250 μm) sample into a 50-ml nickel crucible. Add 20 g of sodium hydroxide pellets to the sample. Cover the crucible with a nickel cover and place it in the bottom of the reaction vessel (Fig. 1). Flush the vessel with pure argon for 10 min

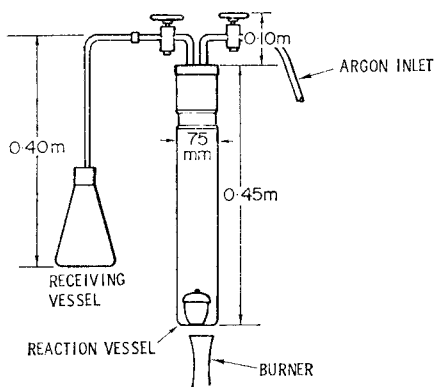


FIG. 1.—System used to determine nitrogen in boron nitride.

at a rate of 500 ml/min. Place 100 ml of fresh 1% boric acid solution in the receiving flask and start heating the reaction vessel with the Meker burner. The heat of the flame should be sufficient to melt the pellets but not high enough to cause fuming. The reaction should be complete after 20 min heating. Heat the sides of the reaction vessel gently to evaporate any condensed moisture. Continue the gas flow through the tube for another 20 min. Remove the boric acid receiver and titrate the ammonia with 0.1*M* hydrochloric acid to the Methyl Purple end-point.

## DISCUSSION

*Boron*

Quantitative decomposition of BN and conversion of the boron into boric acid or an alkaline borate must be accomplished. Boron nitride is not readily attacked by mineral acids, so an alkaline fusion must be used. Fusion can be accomplished in platinum over an efficient gas burner, but heating is not uniform. Spattering and creeping of the melt over the edge of the crucible are sources of error. Use of a muffle furnace seemed to prevent creeping of the melt, presumably because heating was more uniform. Best results were obtained at a muffle temperature of 900°. The fused material was readily removed from the platinum with distilled water. Fusions were conducted with sodium or potassium carbonate, alone or mixed with sodium nitrate. Best results were obtained with sodium carbonate alone. Nitrates attacked the platinum, causing contamination.

Nitrogen, in the form of cyanate or ammonium compounds, may interfere in the final titration of boric acid; therefore, the behaviour of nitrogen during the fusion step was of interest. Fusion of BN with potassium carbonate produces potassium cyanate,<sup>1</sup> and the assumption was made that sodium carbonate would react in a similar fashion. Sodium cyanate should decompose at 900°, releasing nitrogen from the fused mass. To confirm this, samples of BN were fused with sodium carbonate for varying lengths of time at 900°, and the nitrogen content of the fused material determined by activation analysis.<sup>10</sup> The nitrogen content of the mass was inversely proportional to the fusion time, and virtually all nitrogen was gone after 20 min.

Carbon dioxide had to be removed before the titration. Boiling with acid under reflux was unsuccessful because carbon dioxide was reabsorbed in the condensed water. Boiling the solutions for several minutes in covered beakers removed carbon dioxide without loss of boron, confirming the observation of Blumenthal.<sup>3</sup>

A recording titrator is preferable to reduce the end-point errors; colour indicators are less satisfactory.

To check the accuracy of the boron determination, purified boric acid was carried through all the steps of the procedure as described for BN. Six determinations were made on a sample of boric acid, purified and supplied privately by New Brunswick Laboratory. A boron value of  $17.49 \pm 0.04\%$  was obtained, which agrees well with the theoretical value of 17.48%.

*Nitrogen*

For determination of nitrogen in BN, the nitrogen must be quantitatively released from the compound and measured in pure form. A modified Dumas procedure, using sodium metal, was tried and abandoned when poor results were obtained. Fusions with sodium hydroxide to form ammonia were tried in Pyrex and quartz, but container life was very short—usually one determination. An excessive amount of the alkali reacted with the container at the temperature required for reaction with the BN. Poor precision resulted, and the vigorous reaction with silica often carried over alkaline particles into the receiving flask.

Since quartz alone did not stand up under the caustic attack, a covered nickel crucible was placed inside a quartz tube (Fig. 1) and this system worked well. The rather long tube was necessary since a shorter version gave consistently high results, which were attributed to carry-over of sodium hydroxide droplets. However, "conditioning" of this longer tube was required. Unexplained low answers were obtained in the initial runs with any new tube. After two or three runs with the same crucible in the same quartz vessel, nitrogen values became reproducible. At this point, the apparatus was considered "conditioned" and good values were obtained until complete mechanical failure occurred.

TABLE I.—ANALYSES OF APBN

| Boron, %           | Nitrogen, % |
|--------------------|-------------|
| 43.6               | 55.8        |
| 43.4               | 55.8        |
| 43.6               | 55.7        |
| 43.3               | 55.6        |
| 43.3               | 56.0        |
| 43.3               | —           |
| 43.3               | —           |
| 43.3               | —           |
| Average 43.4 ± 0.1 | 55.8 ± 0.1  |

### Results

Excellent precision was obtained when these methods were used to analyse APBN, the most pure BN available. Table I lists the results obtained on multiple runs of this material.

The agreement between these averages and the theoretical values, 43.56% boron and 56.44% nitrogen, is excellent considering the presence of oxygen (found by activation analysis). Since the oxygen is probably present as  $B_2O_3$ , the smaller deviation in the case of boron is to be expected.

### Application

These methods have shown their versatility in the analysis of all types of commercial BN products. Table II tabulates the results obtained on three samples ranging from pure to impure BN. Sample

TABLE II

| Sample | Boron, % | Nitrogen, % |
|--------|----------|-------------|
| SF 2   | 38.8     | 44.8        |
| HH     | 36.6     | 39.5        |
| UC     | 43.4     | 55.4        |

UC, a hot-pressed BN containing  $B_2O_3$  as a binder, was analysed a number of times and the precision was good:  $\pm 0.1\%$  for B, and  $\pm 0.1\%$  for N. The deviation became somewhat larger for the more impure SF 2:  $0.1\%$  for B and  $\pm 0.3\%$  for N. Sample HH, consisting of very impure BN fibres, was so inhomogeneous that statistical data were not calculated.

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**Summary**—Improved techniques are described for the determination of boron and nitrogen in pure boron nitride. Controlled fusion of boron nitride with sodium carbonate in a muffle furnace is followed by a potentiometric titration of the boric acid. A special quartz vessel is described for the determination of nitrogen. The boron nitride is fused with sodium hydroxide and the resulting ammonia is swept into a receiver and titrated with standard hydrochloric acid. Boron and nitrogen values with their standard deviation are given for a typical pure boron nitride.

**Zusammenfassung**—Verbesserte Vorschriften für die Bestimmung von Bor und Stickstoff in reinem Bornitrid werden beschrieben. Zuerst wird das Bornitrid mit Natriumcarbonat in einem Muffelofen geschmolzen, dann die Borsäure potentiometrisch titriert. Ein spezielles Quarzgefäß zur Stickstoffbestimmung wird beschrieben. Das Bornitrid wird mit Natriumhydroxid geschmolzen, das gebildete Ammoniak in ein Auffanggefäß gespült und mit eingestellter Salzsäure titriert. Für ein typisches reines Bornitrid werden Bor- und Stickstoffwerte mit ihren Standardabweichungen angegeben.

**Résumé**—On décrit des techniques améliorées pour le dosage du bore et de l'azote dans le nitrure de bore pur. La fusion contrôlée du nitrure de bore avec du carbonate de sodium dans un four à moufle est suivie d'un titrage potentiométrique de l'acide borique. On décrit un récipient spécial en quartz pour le dosage de l'azote. L'azoture de bore est fondu avec de la soude et l'ammoniac résultant est balayé dans un récepteur et titré à l'acide chlorhydrique normalisé. On donne les valeurs pour le bore et l'azote avec leur écart type pour un nitrure de bore pur caractéristique.



## REFERENCES

1. J. R. Partington, *A Textbook of Inorganic Chemistry*, 6th Ed. Macmillan, London, 1950.
2. M. D. Lyutaya, T. N. Nazarchuk and K. D. Modylevskaya, *USSR Patent* 142805, Dec. 28, 1961, Appl. Mar. 20, 1961.
3. H. Blumenthal, *Anal. Chem.*, 1951, **23**, 992.
4. O. H. Kriege, *The Analyses of Refractory Borides, Carbides, Nitrides, and Silicates*, Los Alamos Scientific Laboratory Report, LA 2306, 1959.
5. A. S. Lapteva, E. S. Bondarevskaya and E. N. Merkulova, *Ind. Lab., USSR (English Trans.)*, 1968, **34**, 1310.
6. B. Ormont and A. Samoïlov, *Z. Anal. Chem.*, 1935, **102**, 20.
7. I. G. Shafran and R. A. Levinson, *J. Appl. Chem., USSR (English Trans.)*, 1940, **13**, 1885.
8. M. V. Kharitonova, *Tr. Vses. Nauchn.-Issled. Inst. Abrazivov Shlefovaniya (English Trans.)*, 1967, No. 4, 58.
9. E. W. Berter, R. H. Wynne, W. F. Harris, M. I. Mistrik and F. P. Byre, paper presented at the Pittsburgh Conference of Anal. Chem., 4-8 March 1957.
10. B. T. Kenna, personal communication, 1969.

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### An improved colorimetric determination of vanadium in geochemical prospecting samples

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IN THE COURSE of a geochemical survey, rapid determinations of vanadium may be required on large numbers of samples, and a precision of  $\pm 25\%$  at the 95% confidence level is adequate. The colorimetric phosphotungstate method employed by the U.S. Geological Survey<sup>1</sup> can be used over the range 100-4000 ppm vanadium. In some cases the yellow solutions obtained by following the recommended procedure are difficult to compare with standards, owing to suspensions of potassium phosphotungstate<sup>2,3</sup> or to the presence of other coloured cations. This paper describes how the sensitivity and selectivity of the method can be improved by substituting sodium hydrogen sulphate for the potassium compound during fusion of the sample, and by extracting the phosphotungstovanadic acid complex into isobutyl methyl ketone (IBMK).

## EXPERIMENTAL

*Reagents*

Use distilled water and analytical-grade reagents throughout the procedure.

*Sodium hydrogen sulphate*, fused and powdered.

*Nitric acid*, sp. gr. 1.42.

*Diluted nitric acid* (1 + 3).

*Orthophosphoric acid*, sp. gr. 1.75.

*Sodium tungstate dihydrate solution*, 5% w/v.

*Standard vanadium solution*, 100  $\mu\text{g}/\text{ml}$ . Dissolve 0.2296 g of dried ammonium metavanadate in a mixture of 100 ml of water with 30 ml of diluted nitric acid (1 + 3). Dilute to 1 litre with water and mix.

*Isobutyl methyl ketone*.

*Procedure*

Transfer 0.20-g portions of -100 mesh samples into a series of borosilicate test-tubes. Peats, certain soils and materials rich in organic matter should be ignited at 450° overnight so that residual tars or stable humic compounds do not interfere with the determination at a later stage. Add 1 g of powdered sodium hydrogen sulphate to each portion of sample, mix, heat to melt the flux then continue heating at dull red heat for 3 min. Allow the tube to cool, then leach the melt with 6 ml of diluted nitric acid (1 + 3), warming as necessary until the melt is reduced to powder. Dilute the solution to 10 ml, mix, and allow sediment to settle.

Transfer 2.0-ml aliquots of each solution to another series of stoppered tubes. Add 1 ml of concentrated nitric acid to each aliquot and heat to boiling for 5 sec. Add 0.3 ml of orthophosphoric

acid and mix, then 2 ml of sodium tungstate solution and mix. Dilute the mixture to 10 ml with water, mix, and heat in a boiling-water bath for 10 min. Cool the tubes, add 1 ml of IBMK to each, shake them vigorously for 20 sec, then allow the phases to separate.

Prepare a series of standard tubes, using known volumes of standard vanadium solution. To each tube add 1 ml of concentrated nitric acid and heat to boiling for 5 sec. Continue as with the samples, extracting the coloured complex into IBMK as described. Compare the colours of the organic phases in the sample tubes with those of the standard series.

For samples with vanadium contents greater than 0.1%, use smaller weights of sample or smaller aliquots of sample solution.

## RESULTS AND DISCUSSION

The proposed procedure was applied to some hundreds of stream sediment and soil samples from various localities, with results ranging from 25 to 1000 ppm of vanadium. Some of the higher and lower values were compared with spectrographic estimates of total vanadium in the samples. These comparisons, together with results on standard samples are recorded in Table I.

TABLE I.—RESULTS OF DETERMINATIONS OF VANADIUM IN GEOLOGICAL SAMPLES

| Sample              | Vanadium, ppm             |         |                            |
|---------------------|---------------------------|---------|----------------------------|
|                     | Published results<br>Mean | Range   | Spectrographic<br>estimate |
| Syenite rock-1*     | 87                        | 50-150  | —                          |
| Sulphide ore-1*     | 192                       | 90-262  | —                          |
| Granadiorite GSP-1† | 52                        | 38-67   | —                          |
| Andesite AGV-1†     | 121                       | 70-171  | —                          |
| Peridotite PCC-1†   | 31.2                      | 21-55   | —                          |
| Dunite DTS-1†       | 18.9                      | 6-52    | —                          |
| Basalt BCR-1†       | 384                       | 120-700 | —                          |
|                     |                           |         | 75, 50                     |
|                     |                           |         | 200, 250                   |
|                     |                           |         | 100, 50                    |
|                     |                           |         | 125, 125                   |
|                     |                           |         | 50, 25, 50, 50             |
|                     |                           |         | 50, 50, 50                 |
|                     |                           |         | 50, 25                     |
|                     |                           |         | 375, 375, 325              |
|                     |                           |         | 375, 375, 375, 350         |
| Stream sediments:   |                           |         |                            |
| Locality A          | —                         | —       | 200                        |
| Locality B          | —                         | —       | 60                         |
| Locality B          | —                         | —       | 500                        |
| Locality B          | —                         | —       | 100                        |
| Locality B          | —                         | —       | 300                        |
|                     |                           |         | 250, 250                   |
|                     |                           |         | 50, 50                     |
|                     |                           |         | 400, 400                   |
|                     |                           |         | 200, 100                   |
|                     |                           |         | 125, 200, 400              |
|                     |                           |         | 250, 125                   |

\* C.A.A.S. standard sample, described by Webber.<sup>4</sup>

† U.S.G.S. standard sample, described by Flanagan.<sup>5</sup>

Standard deviations of 10 ppm about a mean value of 47 ppm and 20 ppm about a mean of 364 ppm were obtained when using the proposed method to determine the vanadium contents of standard samples PCC-1 and BCR-1. The method is suitable for use in a field laboratory by relatively unskilled operators. Accuracy may be improved in a central laboratory by modifying the sample attack and by making more precise measurements of weight, volume, and colour intensity.

The coloured vanadium complex was extracted more cleanly into IBMK than into isobutanol as used by Sherwood and Chapman.<sup>6</sup> Up to 100-fold amounts (relative to vanadium) of copper, nickel, chromium, and cobalt either present in the samples or added as solutions were not extracted into the organic phase under the conditions given. The coloured complex in IBMK is stable for at least a week in a glass-stoppered tube.

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**Summary**—The colorimetric method employed by the U.S. Geological Survey for the determination of vanadium in large numbers of geochemical prospecting samples has been examined. Use of sodium hydrogen sulphate for fusing the samples avoids precipitation of potassium phosphotungstate during colour development. Sensitivity and selectivity of the method are enhanced by extracting the phosphotungstovanadic acid into isobutyl methyl ketone.

**Zusammenfassung**—Das vom U.S. Geological Survey verwendete Verfahren zur Bestimmung von Vanadium in großen Anzahlen geochemischer Prospektierungsproben wurde untersucht. Die Verwendung von Natriumhydrogensulfat zum Schmelzaufschluß der Probe vermeidet das Ausfallen von Kaliumphosphorwolframat während der Farbentwicklung. Die Empfindlichkeit und die Selektivität des Verfahrens werden verbessert, wenn man die Phosphorwolframvanadiumsäure in Isobutyl-methylketon extrahiert.

**Résumé**—On a examiné la méthode colorimétrique employée par le U.S. Geological Survey pour le dosage du vanadium dans des nombres importants d'échantillons de prospection géochimique. L'emploi de sulfate acide de sodium pour la fusion de l'échantillon évite la précipitation de phosphotungstate de potassium durant le développement de la coloration. La sensibilité et la sélectivité de la méthode sont accrues en extrayant l'acide phosphotungstovanadique en méthylisobutyl-cétone.

#### REFERENCES

1. F. N. Ward, H. W. Lakin, F. C. Canney *et al.*, *U.S. Geol. Surv. Bull.*, 1963, No. 1152, 87.
2. E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 251.
3. W. F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds*, 4th Ed., Vol. II, p. 292. American Chemical Society, Washington, D.C., 1965.
4. G. R. Webber, *Geochim. Cosmochim. Acta*, 1965, 29, 229.
5. F. J. Flanagan, *ibid.*, 1969, 33, 81.
6. R. M. Sherwood and F. R. Chapman Jr., *Anal. Chem.*, 1955, 27, 88.

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### Rapid dissolution of sulphide ore for the determination of copper

(Received 9 February 1971. Accepted 16 March 1971)

THAT PERCHLORIC ACID can be used effectively for the dissolution of sulphide ores for the determination of copper was pointed out by Goetz, Diehl and Hach.<sup>1</sup> Not only is the dissolution more rapid and the need to eliminate nitric acid by evaporation avoided, but in contrast to the nitric acid dissolution no bead of elemental sulphur is formed; such sulphur interferes in the subsequent iodometric determination of copper and requires prolonged boiling with nitric acid plus sulphuric acid for removal. We have no evidence that the perchloric acid dissolution method has found acceptance in commercial laboratories but the method has been used for 20 years without incident by the undergraduates studying quantitative analysis at Iowa State University.<sup>2</sup> We have now found that a mixture of equal volumes of 70% perchloric acid and 85% phosphoric acid is even more efficacious for the dissolution of sulphide ores, than is perchloric acid alone.

Such a mixture of perchloric and phosphoric acids was used by Goetz and Wadsworth<sup>3</sup> to dissolve iron ores. Even those ores most recalcitrant to attack by hydrochloric acid are dissolved in 90 sec by this mixture. Again the method has been used by the undergraduates at Iowa State University for 20 years without incident.<sup>4</sup> The method was extended to the dissolution of manganiferous ores by Knoeck and Diehl,<sup>5</sup> the process providing in addition a convenient oxidation of the manganese to the tervalent state, ready for titrimetric or spectrophotometric determination.

Dissolution of a sulphide ore in the boiling perchloric acid-phosphoric acid mixture is complete in 3-5 min, the time depending principally on the amount of heat applied. No elemental sulphur is formed and the phosphoric acid introduced does not interfere in the subsequent iodometric determination of copper. We have checked the method on a typical sulphide-quartz ore (ISU 537) and for the standardization have used pure copper metal dissolved in the same acid mixture. The recommended procedure given below includes directions for the complete determination and takes advantage of the modern improvements in the iodometric method: the use of fluoride to eliminate interference by iron, pH control to eliminate interference by antimony and arsenic, and exchange adsorption with thiocyanate to improve the colour change at the end-point; for the original work dealing with these features see the papers cited in reference 1.

#### *Recommended procedure*

Transfer an accurately weighed sample containing 0.25-0.30 g of copper to a 500-ml conical flask. Add 15 ml of a mixture of equal volumes of 70% perchloric acid and 85% phosphoric acid. Swirl the mixture until all particles are wetted. Place a short-stem 60° funnel or an air-condenser<sup>6</sup> in the neck of the flask. Heat vigorously and then adjust the heat so that reflux occurs on the walls of the flask but no pronounced, heavy, white fumes of perchloric acid leave the flask. The sample will dissolve in 3-5 min. After the sample has dissolved except for the silica present, cool for about 3 min. Add 50 ml of water through the condenser, mix well, heat to boiling and boil gently for 4-5 min to remove any free chlorine present. Cool to room temperature.

Add dilute ammonia (1 + 1) until the deep blue of the tetra-ammine copper(II) ion appears. Add just enough dilute sulphuric acid (1 + 10) to restore the colour of the aquo-ion. The pH at this point will be 4.7-5.0; until experience is gained it may be checked with a pH-meter. Add 2 g of crystalline ammonium hydrogen fluoride and mix thoroughly. Add 2 g of potassium iodide, mix, and titrate immediately with 0.1N sodium thiosulphate. Just before the end-point add 2 ml of 1% starch solution and continue the titration until the blue starch-iodine colour returns rather slowly after the addition of each drop of thiosulphate. Add 2 g of potassium thiocyanate and then titrate dropwise to the final, abrupt disappearance of the blue colour.

To standardize, lightly sand-paper copper electrical wire to remove any oxide coating and wipe clean with a dry cloth. Take samples of 0.25-0.30 g and apply the procedure.

### RESULTS AND DISCUSSION

The method was checked on ISU 537, Copper Sulfide Ore, a thoroughly blended mixture of 200-mesh, specimen-grade chalcocopyrite (from Butte, Montana) and 400-mesh quartz (Saint Peter formation, Illinois). Found: 31.83, 31.77, 31.87, 31.82, 31.82, 31.77, 31.69, 31.76, 31.78% Cu; average 31.79% standard deviation 0.052%. Earlier value (perchloric acid dissolution method<sup>1</sup>): 31.76% Cu.

The samples dissolved smoothly in about half the time required with perchloric acid alone (with which bumping may occur). In the new method iron is masked as the colourless phosphate or pyrophosphate slightly-dissociated ion and the adjustment of pH is much easier because no iron hydroxide is precipitated during the neutralization.

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**Summary**—A mixture of equal volumes of perchloric acid and phosphoric acid is an excellent solvent for sulphide ores preliminary to the determination of copper. The dissolution is rapid, no bumping occurs, and the visual adjustment of pH prior to the iodometric determination of copper is easier.

**Zusammenfassung**—Ein Gemisch aus gleichen Volumina Überchlorsäure und Phosphorsäure ist ein ausgezeichnetes Lösungsmittel für Sulfiderze vor der Kupferbestimmung. Die Auflösung geht rasch ohne Siedeverzüge vor sich und die visuelle pH-Einstellung vor der jodometrischen Kupferbestimmung ist einfacher.

**Résumé**—Un mélange à volumes égaux d'acide perchlorique et d'acide phosphorique est un solvant excellent pour les minerais sulfurés

préalablement au dosage du cuivre. La dissolution est rapide, il n'y a pas de soubresauts, et l'ajustage visuel du pH avant la détermination iodométrique du cuivre est plus aisé.

#### REFERENCES

1. C. A. Goetz, H. Diehl and C. C. Hach, *Anal. Chem.*, 1949, **21**, 1520.
2. H. Diehl, *Quantitative Analysis*, p. 250. Oakland Street Science Press, Ames, Iowa, 1970.
3. C. A. Goetz and E. P. Wadsworth, Jr., *Anal. Chem.*, 1956, **28**, 375.
4. H. Diehl, *op. cit.*, p. 232.
5. J. Knoeck and H. Diehl, *Talanta*, 1967, **14**, 1083.
6. H. Diehl, *op. cit.*, p. 92, Fig. 7-18.

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### Determination of 0.01-0.1% of samarium in 40-100 mg of lead chloride

(Received 8 January 1971. Accepted 11 March 1971)

IN ORDER to investigate the properties of lead chloride crystals that had been doped with rare earths, it was necessary to determine Sm in lead chloride at the 0.01-0.1% level. Emission spectrography with a d.c. carbon arc was not sensitive enough and the desired Sm-level was too near to the detection limit of X-ray fluorescence. Moreover with the latter technique it seemed possible that the influence of lead in the determination of Sm might be different for the lead chloride crystals and the calibration samples obtained by mixing crystalline lead chloride with a samarium compound. It was therefore decided that a chemical method had to be developed. Some of the work done on this is described here.

#### EXPERIMENTAL

##### *Apparatus and reagents*

Photometric determinations were made at 552 nm in 10-mm cells. For the electrolytic separation of Sm and Pb we used the apparatus shown in Fig. 1, a modification of the apparatus described earlier.<sup>1</sup> It contains about 6 ml of pure mercury as cathode (surface about 600 mm<sup>2</sup>) and a spiral platinum anode. The stirrer paddle floats on the surface of the mercury and stirs both the aqueous phase and the surface of the mercury. All reagents were of sufficient purity, and solutions were stored in polythene bottles.

##### *Preliminary investigations*

From literature research it was concluded that a spectrophotometric determination of Sm should be the best approach to the solution of our problem. The most sensitive determination found was that described by Shibata.<sup>2</sup> Sm reacts with PAN to give a 1:2 complex which can be extracted with diethyl ether. However, we found that more than 50 µg of lead interferes with the determination of Sm and has to be removed.

To eliminate the interference of lead several methods were tried, including ion-exchange, extraction and masking. None of these was satisfactory. Finally we found the electrolytic separation with a mercury pool cathode suitable for our purpose.

##### *Procedure*

A calibration curve was prepared according to the following procedure. Weigh about 100 mg of powdered lead chloride, add 1 ml of 6M hydrochloric acid, 2.5-12.5 ml of Sm solution (5 µg/ml) and if necessary water to a total volume of about 14 ml. Dissolve the lead salt by heating to boiling and by stirring. Add 5 ml of a solution which is 2.5M in sodium acetate and 0.5M in sodium hydroxide, to give a pH of about 5. Cool and add 5 ml of a 5% hydroxylamine hydrochloride solution and dilute in a standard flask to 25 ml. Take 12-15 ml of this solution into the electrolysis vessel and electrolyse for 45 min at 2-2.5 V and 50-100 mA. Transfer 10 ml of the electrolysed solution into a 100-ml Erlenmeyer flask, add 1 ml of 6M hydrochloric acid and 10 ml of water and boil for 10 min, while bubbling nitrogen through the solution. Transfer the cooled solution into a 100-ml separatory funnel, with Teflon stop-cock and glass stopper, add water to a total volume of about 20 ml and

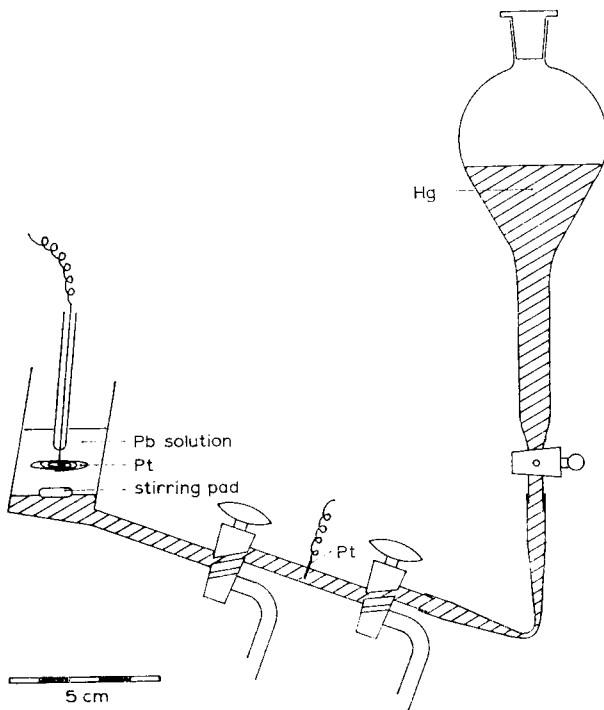


FIG. 1.—Electrolysis vessel.

1 ml of a 0.1% PAN solution in ether. Shake and add 10 ml of a buffer of pH = 10, (0.5M in ammonium chloride and 2.0M in ammonia) to give pH = 9. Shake and after 10 min add 11 ml of distilled ether, shake again vigorously for 2 min and set aside to separate. Transfer the organic layer into a centrifuge tube, add ether (shaken with the buffer pH = 10) to a total volume of 10 ml, centrifuge the solution and measure at 552 nm in 10-mm cells against a blank. Take care to measure between 20 and 60 min after the extraction.

For the blank, take 1 ml of Sm solution (5  $\mu\text{g/ml}$ ) and 1 ml of 6M hydrochloric acid in a 100-ml separatory funnel and carry it through the extraction starting at the addition of water to a total volume of about 20 ml. The use of 1 ml of the Sm solution for the blank is necessary because irregularities are found if no Sm is present.

### RESULTS AND DISCUSSION

The calibration curve is described by the equation  $A = 0.031/\mu\text{g Sm}$ . The standard deviation in the absence of lead and without electrolysis was 0.2  $\mu\text{g}$  (14 variates). In the presence of lead and with electrolysis we found a standard deviation of 0.5  $\mu\text{g}$  (6 variates). Unfortunately, the sample crystals, doped with Sm, were highly inhomogeneous. In order to test the reproducibility of the method applied to these samples, we dissolved 40–100 mg of the sample. For the dissolution and the preparation of the electrolysis solution we used double the amount of the reagents mentioned above and diluted to 50 ml. From a solution thus obtained, three parallel runs (electrolysis and spectrophotometric determination) were made. We made determinations on six crystal samples and found values between 0.01 and 0.1% of Sm. The pooled standard deviation was about 1  $\mu\text{g}$  (12 variates).

Under the conditions chosen, the anodic oxidation of lead to  $\text{PbO}_2$  is prevented by the hydroxylamine hydrochloride. If a higher current is applied or if more lead is present,  $\text{PbO}_2$  is formed even in the presence of the hydroxylamine hydrochloride. The latter compound does not interfere with the spectrophotometric determination. The removal of the reaction products of the electrolysis by boiling and bubbling nitrogen through the solution, is necessary.

We found some modifications of Shibata's procedure to be desirable. We used ether instead of methanol as a solvent for PAN. This leads to a simpler extraction system and probably to more

stable PAN solutions. Furthermore we added ether to make up to final volume to overcome the consequences of the solubility of ether in water. (The magnitude of this solubility is appreciable and depends on temperature.) Finally, we made our measurements at 552 nm instead of at 530 nm because the absorbance of the reagent is much smaller at 552 nm. However, the sensitivity at this wavelength is about 20% less than at 530 nm.

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**Summary**—A method is described for the determination of 5–25  $\mu\text{g}$  of samarium in about 40 mg of lead chloride, based on the removal of the lead by electrolysis and determination of the samarium by extraction with PAN and measurement of the extinction of the complex at 552 nm.

**Zusammenfassung**—Ein Verfahren zur Bestimmung von 5–25  $\mu\text{g}$  Samarium in etwa 40 mg Bleichlorid wird beschrieben. Es beruht auf der elektrolytischen Abscheidung von Blei und der Bestimmung des Samariums durch Extraktion mit PAN und Messung der Extinktion des Komplexes bei 552 nm.

**Résumé**—On décrit une méthode pour le dosage de 5–25  $\mu\text{g}$  de samarium dans environ 40 mg de chlorure de plomb, basée sur l'élimination du plomb par électrolyse et le dosage du samarium par extraction au moyen de PAN et mesure de l'extinction du complexe à 552 nm.

#### REFERENCES

1. NEN 3105-1, Nederlands Normalisatie Instituut, Rijswijk (Z.H), Holland, 1964.
2. S. Shibata, *Anal. Chim. Acta*, 1963, **28**, 388.

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### Synergistic effects in the solvent extraction of zinc with salicylaldoxime

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THE PHENOMENON of synergism in solvent extraction systems containing  $\beta$ -diketones and neutral donors has been extensively investigated.<sup>1</sup> Studies with other chelating agents have been confined to 8-hydroxyquinoline<sup>2</sup> and dimethylglyoxime.<sup>3</sup> Dahl<sup>4</sup> has studied the solvent extraction of various metal ions with salicylaldoxime (HA) and noticed that the extraction of Zn(II) with low concentrations of salicylaldoxime was very poor. We have investigated the solvent extraction of zinc salicylaldoximate and its adducts with heterocyclic bases.

#### EXPERIMENTAL

##### Reagents

All the reagents used were of analytical grade. Salicylaldoxime was used without further purification. Pyridine,  $\alpha$ -picoline,  $\beta$ -picoline, quinoline and isoquinoline were dried and fractionated immediately before use. Benzene was purified by the standard method.<sup>5</sup>

##### Procedure

The pH of the aqueous phase was measured after extraction, preliminary experiments having shown that the buffering capacity of the aqueous phase was insufficient to maintain a constant pH.

All experiments were carried out at  $35 \pm 0.1^\circ\text{C}$ . The initial volumes of both phases were 20.0 ml. The concentration of Zn(II) in the system was  $10^{-4}M$ , and the ionic strength of the aqueous phase was kept constant at  $0.1M$  by using sodium perchlorate ( $0.09M \text{NaClO}_4 + 0.01M$  buffer). The hydrogen ion concentration of the solution was kept constant by using sodium acetate-acetic acid for experiments at pH between 4 and 6 and ammonium chloride-ammonia for pH values above 6.

(Ammonia-acetic acid buffers prepared according to Smith<sup>6</sup> were also employed for the pH range 6-9.)

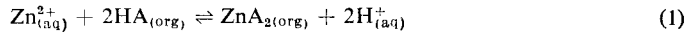
The organic and aqueous solutions were placed in stoppered glass bottles and shaken in a thermostatic bath ( $35 \pm 0.1^\circ\text{C}$ ) for 1 hr. Aliquots were taken from both phases for spectrophotometric estimation of Zn(II) with dithizone.<sup>7</sup> The remaining aqueous phase was taken for pH measurements. The  $K_d$  values were calculated according to the formula

$$K_d = \frac{\text{Total concentration of Zn(II) in the organic phase}}{\text{Total concentration of Zn(II) in the aqueous phase}}$$

### RESULTS AND DISCUSSION

The extraction of metal chelates can be described by a plot of  $\log K_d$  against pH at constant reagent concentration in the organic phase. This gives the number of protons released during the complex formation. It is also described by the plot of  $\log K_d$  against reagent concentration in the organic phase at constant pH, which gives the number of reagent molecules incorporated into the extractable complex.

A plot of  $\log K_d$  vs. pH has a slope of 2, indicating that two protons are released during complex formation. The deviation observed at high pH values is probably due to the formation of negatively charged complexes in the aqueous phase,  $\text{Zn}(\text{Sal})_2^-$ . A plot of  $\log K_d$  against  $\log [\text{HA}]$  at constant pH also gives a slope of 2, indicating that two molecules of HA are required for the complex formation. This also indicates that zinc salicylaldoximate does not form an adduct with excess of reagent. Hence the extraction equilibrium for the zinc-salicylaldoxime system is given by the equation:



The equilibrium constant is given by

$$K_{\text{ex}} = [\text{ZnA}_2]_{\text{org}}[\text{H}^+]^2/[\text{Zn}^{2+}][\text{HA}]_{\text{org}}^2 \quad (2)$$

When no complexes are formed in the aqueous phase the distribution ratio is given by:

$$K_{d_0} = [\text{ZnA}_2]_{\text{org}}/[\text{Zn}^{2+}]_{\text{aq}} \quad (3)$$

From (2) and (3)

$$K_{d_0} = K_{\text{ex}}[\text{HA}]_{\text{org}}^2/[\text{H}^+]^2 \quad (4)$$

A plot of  $\log K_{d_0} + 2 \log [\text{H}^+]$  against  $\log [\text{HA}]$  yields a straight line of slope 2 and an intercept of  $-11.52$  ( $\log K_{\text{ex}}$ ).

Adduct formation with neutral donors can be written as:



with the equilibrium constant

$$K_{\text{ex}} = [\text{ZnA}_2\text{L}_n]_{\text{org}} [\text{H}^+]^2/[\text{Zn}^{2+}][\text{HA}]_{\text{org}}^2 [\text{L}]_{\text{org}}^n \quad (6)$$

and

$$\beta_n = [\text{ZnA}_2\text{L}_n]_{\text{org}} [\text{L}]_{\text{org}}^n/[\text{ZnA}_2]_{\text{org}} \quad (7)$$

and

$$K_d = [\text{ZnA}_2\text{L}_n]_{\text{org}}/[\text{Zn}^{2+}]_{\text{aq}} \quad (8)$$

substitution of  $\beta$  and  $K_{\text{ex}}$  into equation (8) gives:

$$\log K_d [\text{H}^+]^2/[\text{HA}]_{\text{org}}^2 = \log K_{\text{ex}} (1 + \beta_1[\text{L}]_{\text{org}} + \dots + \beta_n[\text{L}]_{\text{org}}^n) \quad (9)$$

Substituting for  $K_{\text{ex}}$  from equation (4):

$$\log K_d/K_{d_0} = \log (1 + \beta_1[\text{L}]_{\text{org}} + \dots + \beta_n[\text{L}]_{\text{org}}^n) \quad (10)$$

$\beta_1, \beta_2, \dots, \beta_n$  are evaluated by the procedures of Sekine and Dyrssen.<sup>8</sup>

Since the partition coefficients of the bases in the organic solvents are low, the concentrations of the bases in the organic phase were obtained by using the formula<sup>9</sup>

$$[\text{B}]_{\text{total}} = [\text{B}]_{\text{org}} \left[ 1 + \frac{1}{P_B} + \frac{1}{P_B K_{\text{BH}}} \right]$$

where  $P_B = [\text{B}]_{\text{org}}/[\text{B}]_{\text{aq}}$  and  $K_{\text{BH}} = [\text{B}][\text{H}^+]/[\text{BH}^+]$ , i.e., the protonation constant of the base.



$P_{13}$  values for pyridine,  $\alpha$ -picoline and  $\beta$ -picoline were assumed to be the same as those of  $\gamma$ -picoline which has a value of 1.6.<sup>10</sup> The  $P_B$  and  $K_{BH}$  values of quinoline and isoquinoline were taken from the data of Irving and Alniami.<sup>11</sup> The calculated  $[B]_{org}$  was used in the plots of  $\log K_d/K_{d_0}$  against  $\log [L]_{org}$ .

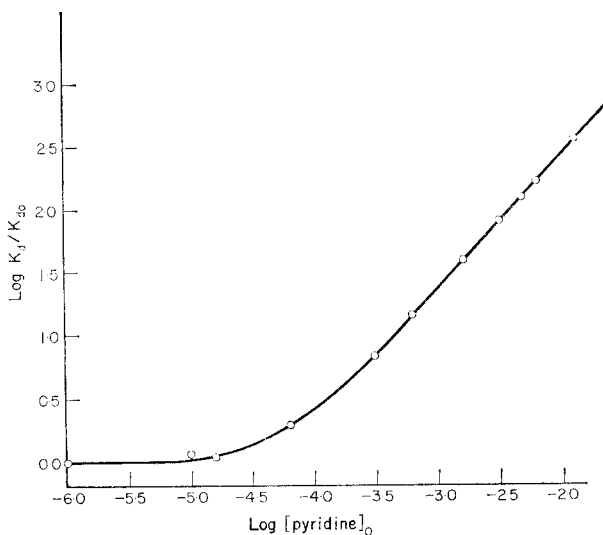


FIG. 1.—Plot of  $\log K_d/K_{d_0}$  vs.  $\log [\text{pyridine}]_o$ :  $[HA] = 0.05M$ ,  $\text{pH} = 6.6$ .

At constant salicylaldehyde concentration of 0.05M and pH of 6.6, Fig. 1 gives the plot of  $\log K_d/K_{d_0}$  against  $\log [L]_{org}$  for pyridine, those for  $\alpha$ -picoline,  $\beta$ -picoline, quinoline and isoquinoline are similar and all the plots give a curve with a limiting slope of unity, and fit the normalized curve  $Y = \log(1 + v)$ ;  $X = \log v$ . The calculated values of  $\log \beta_1$  are given in Table I.

TABLE I.—EQUILIBRIUM CONSTANTS OF ADDUCT FORMATION

| Donor (L)          | $\log \beta_1$ |
|--------------------|----------------|
| Pyridine           | 4.26           |
| $\alpha$ -Picoline | 4.14           |
| $\beta$ -Picoline  | 4.60           |
| Quinoline          | 3.74           |
| Isoquinoline       | 4.08           |

From Table I, it can be seen that the adduct forming tendencies of the heterocyclic bases are in the order  $\beta$ -picoline > pyridine >  $\alpha$ -picoline > isoquinoline > quinoline. These results are in accordance with those of Akaiwa and Kawamoto<sup>9</sup> who studied the effects of pyridine bases in the extraction of metal  $\beta$ -diketonates, and of Irving and Alniami<sup>11</sup> who studied the solvent extraction of metals by mixtures of acetylacetone and quinoline or isoquinoline.

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**Summary**—The extraction of zinc with salicylaldoxime was studied. The adduct-forming tendency of zinc salicylaldoximate with pyridine,  $\alpha$ -picoline,  $\beta$ -picoline, quinoline and isoquinoline was also investigated. This tendency decreases in the order  $\beta$ -picoline > pyridine >  $\alpha$ -picoline > isoquinoline > quinoline.

**Zusammenfassung**—Die Extraktion von Zink mit Salicylaldoxim wurde untersucht. Die Tendenz von Zink-Salicylaldoximat zur Bildung von Addukten mit Pyridin,  $\alpha$ -Picolin,  $\beta$ -Picolin, Chinolin und Isochinolin wurde ebenfalls untersucht. Diese Tendenz nimmt in der Reihenfolge  $\beta$ -Picolin > Pyridin >  $\alpha$ -Picolin > Isochinolin > Chinolin ab.

**Résumé**—On a étudié l'extraction du zinc par la salicylaldoxime. On a aussi examiné la tendance du salicylaldoximate de zinc à former des composés d'addition avec la pyridine, l' $\alpha$ -picoline, la  $\beta$ -picoline, la quinoléine et l'isoquinoléine. Cette tendance décroît dans l'ordre:  $\beta$ -picoline > pyridine >  $\alpha$ -picoline > isoquinoléine > quinoléine.

#### REFERENCES

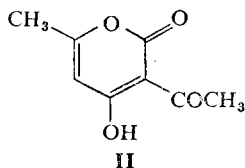
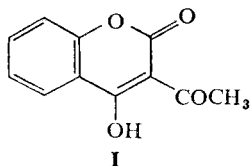
1. Y. Marcus and A. S. Kertes, *Ion-Exchange and Solvent Extraction of Metal Complexes*, p. 818. Wiley, New York, 1969.
2. Fa-Chun Chou, Q. Fernando and H. Freiser, *Anal. Chem.*, 1965, **37**, 361.
3. D. Dyrssen and M. Hennicks, *Acta Chem. Scand.*, 1960, **15**, 47.
4. I. Dahl, *Anal. Chim. Acta*, 1968, **41**, 9.
5. A. Weissberger, *Technique of Organic Chemistry; Organic Solvents*, Vol. VII. Interscience, New York, 1955.
6. T. B. Smith, *Analytical Processes*, 2nd Ed., p. 442. Arnold, London, 1940.
7. G. Charlot, *Colorimetric Determination of Elements, Principles and Methods*, p. 432. Elsevier, London, 1964.
8. T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1727.
9. H. Akaiwa and H. Kawamoto, *ibid.*, 1967, **29**, 1345.
10. H. M. N. H. Irving and N. S. Alniami, *ibid.*, 1965, **27**, 717.
11. *Idem, ibid.*, 1965, **27**, 1671.

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### Dehydroacetic acid as a reagent for the separation and gravimetric determination of copper(II), aluminium and beryllium

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BHAT AND JAIN have used 3-acetyl-4-hydroxycoumarin, (I), for the estimation of titanium(IV), cerium(IV), thorium(IV), uranium(VI) and iron(II),<sup>1</sup> but dehydroacetic acid (II), (2-acetyl-5-hydroxy-3-oxohex-4-enoic acid- $\delta$ -lactone, or 3-acetyl-6-methyl-[2H]-pyran-2,4[3H]-dione) which is structurally related to 3-acetyl-4-hydroxycoumarin, and forms metal complexes, has not been applied in analysis. During our present investigations, we have observed that a precipitate is formed by the addition of an aqueous solution of dehydroacetic acid to aqueous solutions of copper(II) (faint violet), aluminium (white), beryllium (white), cerium(IV) (reddish brown) and vanadium(IV)



(chocolate brown), but no other cations. The precipitation of cerium and vanadium is not quantitative over the pH range 0-12 whereas the precipitation of copper(II), aluminium and beryllium is quantitative within the pH ranges 3.0-6.0, 3.0-6.0 and 7.5-9.5 respectively. Procedures for the gravimetric determination of these three ions have been established.

## EXPERIMENTAL

### Reagents

*Stock solutions of copper(II), aluminium and beryllium.* Prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{BeCO}_3$  (in sulphuric acid), and standardized gravimetrically *via*  $\text{CuCNS}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{BeO}$  respectively.<sup>2</sup>

*Dehydroacetic acid.* The reagent (m.p. 108°) is easily prepared by the self-condensation of ethyl acetoacetate<sup>3</sup> in the presence of sodium hydrogen carbonate. It was used as 1% w/v aqueous solution.

### Procedures

*Copper (II).* Add to about 50 ml of copper(II) sulphate solution containing 1-13 mg of Cu(II) at 40° and pH 3-6, 1.5 ml of reagent solution per mg of Cu(II). Keep the solution at room temperature (20-30°) for about 15 min to coagulate the precipitate, and filter off on a weighed sintered-glass crucible, porosity 3. Wash the precipitate with cold water till free from foreign ions. Dry at 110-120° and weigh as  $\text{Cu}(\text{C}_8\text{H}_7\text{O}_4)_2$ .

The precipitated complex is stable over the temperature range 110-160°. It is soluble in ethanol, acetone, chloroform, carbon tetrachloride and benzene, but decomposes in mineral acids and sodium hydroxide or ammonia.

*Aluminium.* Add to *ca.* 50 ml of the solution containing 2.5-30 mg of  $\text{Al}_2\text{O}_3$ , at 40°, 2.5 ml of reagent solution per mg of Al. Make the solution just basic to Methyl Red and keep it at room temperature for *ca.* 15 min to coagulate the precipitate. Filter off on Whatman No. 41 paper and wash with cold water till free from foreign ions. Ignite at 1100-1200° and weigh as  $\text{Al}_2\text{O}_3$ .

*Beryllium.* To *ca.* 50 ml of solution containing 2-20 mg of Be, at 40°, add 5 ml of reagent solution per mg of Be. Raise the pH to *ca.* 8 (phenolphthalein), and allow the flocculent white precipitate thus obtained to stay at room temperature for about 30 min. Filter off on Whatman No. 40 paper, wash free from foreign ions with water containing 0.1% w/v dehydroacetic acid, and then ignite the precipitate at 900°. Weigh as BeO.

*Aluminium/beryllium mixture.* Add excess of reagent and precipitate and determine the aluminium as above, then increase the pH to 8 and determine the beryllium.

Results are reported in Tables I and II.

TABLE I.—DETERMINATION OF COPPER(II), ALUMINIUM AND BERYLLIUM WITH DEHYDROACETIC ACID

| Copper(II), mg |        |       | Aluminium |                                       |       | Beryllium |                  |       |
|----------------|--------|-------|-----------|---------------------------------------|-------|-----------|------------------|-------|
| Taken          | Found  | Diff. | Taken     | $\text{Al}_2\text{O}_3$ , mg<br>Found | Diff. | Taken     | BeO, mg<br>Found | Diff. |
| 1.270          | 1.250  | 0.020 | 2.59      | 2.55                                  | 0.04  | 2.23      | 2.10             | 0.13  |
| 1.905          | 1.895  | 0.010 | 5.18      | 5.25                                  | 0.07  | 4.45      | 4.50             | 0.05  |
| 2.540          | 2.520  | 0.020 | 7.86      | 7.90                                  | 0.04  | 6.68      | 6.60             | 0.08  |
| 3.175          | 3.168* | 0.007 | 10.35     | 10.40†                                | 0.05  | 9.90      | 9.90*            | 0.00  |
| 5.080          | 5.075§ | 0.005 | 15.58     | 15.56*                                | 0.02  | 14.35     | 14.34*           | 0.01  |
| 6.350          | 6.332‡ | 0.018 | 20.70     | 20.72‡                                | 0.02  | 19.80     | 19.80†           | 0.00  |
| 9.525          | 9.502† | 0.023 | 31.05     | 31.10                                 | 0.05  | 29.80     | 29.70            | 0.10  |

\* Average of 15 estimations.

† Average of 5 estimations.

‡ Average of 2 estimations.

§ Average of 8 estimations.

|| Average of 3 estimations.

TABLE II.—DETERMINATION OF ALUMINIUM(III) AND BERYLLIUM(II) WHEN PRESENT TOGETHER

| Taken, mg                      |       | Found |                                      |     |           | Difference, mg                 |       |
|--------------------------------|-------|-------|--------------------------------------|-----|-----------|--------------------------------|-------|
| Al <sub>2</sub> O <sub>3</sub> | BeO   | pH    | Al <sub>2</sub> O <sub>3</sub><br>mg | pH  | BeO<br>mg | Al <sub>2</sub> O <sub>3</sub> | BeO   |
| 7.86                           | 29.70 | 4.0   | 7.90                                 | 8.3 | 29.50     | +0.04                          | -0.20 |
| 10.35                          | 6.68  | 3.9   | 10.50                                | 8.2 | 6.70      | +0.15                          | +0.02 |
| 15.58                          | 19.80 | 4.2   | 15.50                                | 7.9 | 19.65     | -0.08                          | -0.15 |
| 20.70                          | 14.84 | 3.8   | 20.75                                | 8.5 | 14.40     | +0.05                          | -0.44 |
| 15.58                          | 29.70 | 3.9   | 15.50                                | 8.7 | 29.90     | -0.08                          | +0.20 |
| 10.35                          | 19.80 | 4.3   | 10.35                                | 8.2 | 19.95     | 0.00                           | +0.15 |
| 31.05                          | 19.80 | 4.2   | 30.90                                | 8.2 | 19.70     | -0.15                          | -0.10 |

## RESULTS AND DISCUSSION

*Effect of pH*

It was observed that the precipitation of copper(II), aluminium and beryllium complexes with dehydroacetic acid is quantitative within the pH ranges 3.0-6.0, 3.0-6.0 and 7.5-9.5 respectively.

*Interferences due to the foreign ions*

*Determination of copper(II).* It was found that up to 20-fold amounts of acetate, tartrate, citrate, borate, fluoride, nickel, cobalt, zinc, cadmium, manganese(II), calcium, magnesium, silver, molybdenum(VI), arsenic(V), chromium(III), cerium(III), thorium and 5-fold amounts of dioxouranium(VI) do not interfere. Oxalate and phosphate interfered because of the formation of insoluble precipitates with copper(II) at the pH of the estimation; bismuth, antimony(III) and tin(II) interfered because of their hydrolysis. Aluminium, cerium(IV) and vanadium(IV) interfered because they formed insoluble complexes with dehydroacetic acid, and iron(II), iron(III) and uranium(VI) (in greater than 7-fold excess) interfered because of the adsorption of their coloured complexes on the precipitate. Stronger complexing agents such as EDTA and ethylenediamine prevented the precipitation of copper(II)-dehydroacetic acid complex.

*Determination of aluminium.* The following ions in 10-fold amount did not interfere: acetate, tartrate, citrate, nickel, cobalt(II), zinc, manganese(II), cadmium, calcium, magnesium, beryllium, mercury(II), cerium(III) and chromium(III). Borate, phosphate, fluoride, oxalate, vanadate, molybdate and arsenate interfered by forming insoluble aluminium complexes, whereas bismuth, antimony(III) and tin(II) interfered because of their hydrolysis. Iron(II) and (III), and uranium(VI) complexes are adsorbed by the precipitated complex, while vanadium(IV), copper(II) and cerium(IV) form insoluble dehydroacetic acid complexes, and hence interfere.

*Determination of beryllium.* Because of the high pH required for the complete precipitation of Be most of the metal ions studied interfered because of their hydrolysis to form insoluble complexes. Acetate, tartrate and citrate when present in 10-fold excess did not cause any interference. The interference of iron(II), nickel, cobalt(II) and zinc could be eliminated by using 1 g of tartrate; calcium and magnesium did not interfere in the presence of 1 g of citric acid.

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**Summary**—Dehydroacetic acid is proposed as a reagent for the gravimetric determination of copper(II), aluminium and beryllium at pH 3.0-6.0, 3.0-6.0 and 7.5-9.5 respectively. Copper is weighed as the complex  $\text{Cu}(\text{C}_8\text{H}_7\text{O}_4)_2$ . Aluminium and beryllium are weighed as  $\text{Al}_2\text{O}_3$  and BeO. The reagent is easy to prepare.

**Zusammenfassung**—Dehydroessigsäure wird als Reagens zur gravimetrischen Bestimmung von Kupfer(II), Aluminium und Beryllium bei pH 3,0-6,0, 3,0-6,0 bzw. 7,5-9,5 vorgeschlagen. Kupfer wird in Form des Komplexes  $\text{Cu}(\text{C}_8\text{H}_7\text{O}_4)_2$  gewogen, Aluminium und Beryllium als  $\text{Al}_2\text{O}_3$  bzw. BeO. Das Reagens ist leicht herzustellen.

**Résumé**—On propose l'acide déhydroacétique comme réactif pour le dosage gravimétrique du cuivre(II), de l'aluminium et du beryllium à pH 3,0–6,0; 3,0–6,0 et 7,5–9,5 respectivement. On pèse le cuivre sous forme de complexe  $\text{Cu}(\text{C}_8\text{H}_7\text{O}_4)_2$ . L'aluminium et le beryllium sont pesés à l'état  $\text{Al}_2\text{O}_3$  et  $\text{BeO}$ . Le réactif est aisé à préparer.

## REFERENCES

1. A. N. Bhat and B. D. Jain, *Talanta*, 1961, **5**, 271, 1961, **4**, 13; *J. Less-Common Metals*, 1961, **3**, 259; *J. Inorg. Nucl. Chem.*, 1961, **23**, 136; *Proc. Indian Acad. Sci.*, 1961, **53A**, 147.
2. A. I. Vogel, *A Text Book of Quantitative Analysis*, 3rd Ed. Longmans, London, 1962.
3. F. Arndt, B. Eistert, H. Scholz and E. Aron, *Ber.*, 1936, **69B**, 2373.

## PAPERS RECEIVED

---

- Determination of the absolute  $pK_a$  of acetic and benzoic acid in pyridine:** L. M. MUKHERJEE and RONALD S. SCHULTZ. (23 June 1971)
- Statocalcein: A stable calcein indicator for the EDTA titration of calcium:** WILLIAM C. HOYLE and HARVEY DIEHL. (24 June 1971)
- Microdosage du silicium dans les composés organiques:** E. DEBAL. (28 June 1971)
- Removal of graphite by oxidation with perchloric acid plus periodic acid. Inapplicability to the spectrophotometric determination of manganese in steel:** JAMES A. GAUNT and HARVEY DIEHL. (2 July 1971)
- Applications de l'iodométrie coulométrique aux dosage microanalytiques de l'arsenic, de l'antimoine et du cuivre dans les composés organiques:** M. BIGOIS. (12 July 1971)
- Applications des méthodes coulométriques aux dosages microanalytiques du manganèse et du chrome dans les composés organiques:** M. BIGOIS. (12 July 1971)
- Spectrophotometric determination of nitrilotriacetic acid as a nickel chelate:** PETR VAŇURA and LIBOR KUČA. (19 July 1971)
- Trennung anorganischer Phosphate an Anionenaustauscher-Fertigplatten:** H. KROSCHWITZ, S. FERENCZI and E. PUNGOR. (19 July 1971)
- Application of *N*-(2-acyl-1,3-indandione-1-hydrazone)trialkylammonium iodides—a new group of reagents for the carbonyl group:** M. K. BACHLAUS and K. L. MENARIA. (21 July 1971)
- Potentiometric method for the successive titration of sulphide and dissolved sulphur in polysulphide solutions:** SANAE IKEDA, HIROMU SATAKE, TAKEO HISANO and TOSHIO TERAZAWA. (26 July 1971)
- Determination of phosphorus in lubricating oils by cool-flame emission spectroscopy:** W. N. ELLIOT, C. HEATHCOTE and R. A. MOSTYN. (2 August 1971)
- Thermodynamic proton-ligand stability constants of *N*-phenylbenzohydroxamic acids and benzo-hydroxamic acid:** Y. K. AGRAWAL and S. G. TANDON. (2 August 1971)
- Considerations on the interpretation of the oxidation-reduction phenomenon:** GH. GHIMICESCU. (4 August 1971)
- Univalent cation-exchange in organic solvent-water and organic solvent-water-phenol mixtures:** J. G. JONES and J. D. R. THOMAS. (4 August 1971)
- Recent developments in fluorimetric and photometric determinations of the rare earths:** MAUREEN W. MATKOVICH. (6 August 1971)
- Spectrophotometric estimation of molybdenum with disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate:** ANIL K. CHAKRABARTI and SASWATI P. BAG. (9 August 1971)
- Analysis of metals by solid-liquid separation after liquid-liquid extraction. Spectrophotometric determination of palladium(II) by extraction of palladium dimethylglyoximate with melted naphthalene:** TAITIRO FUJINAGA, MASATADA SATAKE and TATSUO YONEKUBO. (9 August 1971)
- Spectrophotometric determination of vanadium with thiosalicylamide:** H. SIKORSKA-TOMICKA and M. LEWICKA. (12 August 1971)
- Synthesis and ion-exchange properties of thermally stable stannic selenite: Separation of  $Cu^{2+}$  from  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Ga^{3+}$  and  $In^{3+}$ ; separation of  $Fe^{3+}$  from  $Pb^{2+}$ ,  $Sc^{3+}$  and of  $Sc^{3+}$  from  $VO^{2+}$ :** MOHSIN QURESHI and SYED ASHFAQ NABI. (12 August 1971)
- Stability constants of complexes of *N*-arylhydroxamic acids with some bivalent metal ions:** J. P. SHUKLA and S. G. TANDON. (13 August 1971)

**Titrimetric determination of microgram amounts of manganese after amplification:** J. W. HAMYA and A. TOWNSHEND. (17 August 1971)

**Determination of trace elements in metals with alloys by atomic-absorption spectroscopy, using an induction-heated graphite "well" furnace as atom source:** J. B. HEADRIDGE and DAVID RISSON SMITH. (19 August 1971)

**Neutron-activation determination of thorium in zircon:** H. B. DESAI, R. PARTHASARATHY and M. SANKAR DAS. (26 July 1971)

**On the electrolytic accumulation of anions at hanging mercury drop electrodes (HMDE):** A. BARANSKI and Z. GALUS. (27 July 1971)

## SUMMARIES FOR CARD INDEXES

**Zum Konvergenzbereich der iterativen Ermittlung sukzessiver Protonierungskonstanten und zu deren relativer Reihenfolge:** D. WAGLER and E. HOYER, *Talanta*, 1971, **18**, 991. (Sektion Chemie der Karl-Marx-Universität, Leipzig, DDR.)

**Summary**—Two independent methods are described for calculation of protonation constants of tribasic ligands: the logarithmic iterative procedure as well as the numerical method is used for the estimation of the relative sequence of  $pK$  or  $\log K$  values respectively from the pH differences at  $\bar{n} = 0.5$ , 1.5 and 2.5 on the protonation curve. The convergence limits for the iterative procedure are given as a function of these pH differences. Closed expressions for the critical values of the iteration are presented for any pair of pH and  $\bar{n}$ .

**Cation-exchange separation of uranium from other elements in tetrahydrofuran-nitric acid media containing trioctylphosphine oxide:** M. M. KHATER and J. KORKISCH, *Talanta*, 1971, **18**, 1001. (Analytical Institute, University of Vienna, IX Währingerstrasse 38, Austria.)

**Summary**—The batch distribution coefficients of Cu(II), Zn, Cd, Fe(III), Hg(II), Mg, Co(II), Ni, Pb, Ca and Bi were determined on the strongly acidic cation-exchange resin Dowex 50  $\times$  8 in 0.1M trioctylphosphine oxide in tetrahydrofuran-5% 12M nitric acid. In this mixture all these metal ions, except Bi, have high  $K_d$ -values and can be separated quantitatively from uranium which has a distribution coefficient of 0.1. Mixtures of U with Cu, Ni, Co, Cd or Fe were analysed to test the applicability of such separations. Different titrimetric and spectrophotometric methods were used to determine the elements subsequent to their separation from uranium on ion-exchange columns. The results show that accurate and effective separations can be achieved.

**Determination of indium and thallium in indium-thallium alloys:** MELVIN J. TSCHETTER, ROBERT Z. BACHMAN and CHARLES V. BANKS, *Talanta*, 1971, **18**, 1005. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

**Summary**—The thallium-indium alloys were dissolved in sulphuric acid (1 + 1). In this medium thallium remained in the univalent state and could be determined directly, without a separation, by an oxidation-reduction titration with potassium bromate. The indium was determined directly with an EDTA titration. Ascorbic acid was added to maintain the thallium in the univalent state, which did not interfere. Ascorbic acid also masked any interfering trivalent thallium by effectively reducing it to the univalent state. Sharp end-points were obtained for both titrations, which were carried out in the temperature range of 50–95°. The method offers excellent precision and accuracy.



ОБЛАСТЬ КОНВЕРГЕНЦИИ ИТЕРАТИВНОГО  
РАССЧЁТА ПОСЛЕДОВАТЕЛЬНЫХ КОНСТАНТ  
ПРОТОНАЦИИ И ИХ ОТНОСИТЕЛЬНЫЙ ПОРЯДОК:

D. WAGLER and E. HOYER, *Talanta* 1971, **18**, 991.

**Резюме**—Описана два независимых метода расчёта констант протонации трёхосновных лигандов: логарифмический итеративный метод так как и цифровой метод Б, использованы для определения относительного порядка значений  $pK$  или  $\lg K$ , соответственно, из разниц  $pH$  при  $\bar{n} = 0.5; 1.5; 2.5$  на кривой протонации. Пределы конвергенции итеративного метода приведены в зависимости от этих разниц  $pH$ . Замкнутые выражения для критических значений итерации приведены для каждой пары  $pH$  и  $\bar{n}$ .

КАТИОНООБМЕННОЕ ОТДЕЛЕНИЕ УРАНА ОТ  
ДРУГИХ ЭЛЕМЕНТОВ В СРЕДАХ  
ТЕТРАГИДРОФУРАНА И АЗОТНОЙ КИСЛОТЫ,  
СОДЕРЖАЩИХ ТРИОКТИЛФОСФИНОКСИД:

M. M. KNATER and J. KORKISCH, *Talanta* 1971, **18**, 1001.

**Резюме**—Определены периодические коэффициенты распределения  $Cu(II)$ ,  $Zn$ ,  $Cd$ ,  $Fe(III)$ ,  $Hg(II)$ ,  $Mg$ ,  $Co(II)$ ,  $Ni$ ,  $Pb$ ,  $Ca$ , и  $Bi$  на сильнокислой катионообменной смоле Дауекс  $50 \times 8$  в  $0,1M$  растворе триоктилфосфиноксида в тетрагидрофуране— $5\%$   $12M$  азотной кислоте. В этой смеси вышеупомянутые ионы металлов, за исключением  $Bi$ , имеют большие значения  $K_d$  и могут быть отделены количественно от урана, коэффициент распределения которого равен  $0,1$ . Анализированы смеси  $U$  с  $Cu$ ,  $Ni$ ,  $Co$ ,  $Cd$  или  $Fe$  с целью испытать применимость таких сепараций. Разные методы титриметрического и спектрофотометрического анализа использованы для определения элементов после их отделения от урана на колонках ионообменника. Результаты показывают что метод позволяет получать точные и эффективные разделения.

ОПРЕДЕЛЕНИЕ ИНДИЯ И ТАЛЛИЯ В СПЛАВАХ  
ИНДИЯ И ТАЛЛИЯ:

MELVIN J. TSCHETTER, ROBERT Z. BACHMAN and CHARLES V. BANKS, *Talanta*, 1971, **18**, 1005.

**Резюме**—Сплавы индия и таллия растворяли в серной кислоте (1 + 1). В этой среде таллий остается в одновалентной форме и может определяться непосредственно, без разделения, окислительно-восстановительным титрованием с броматом калия. Индий определяли непосредственно титрованием с ЭДТА. Раствору добавляли аскорбиновую кислоту для сохранения таллия в одновалентной форме, которая не мешает определению. Аскорбиновая кислота также маскирует мешающий трехвалентный таллий, восстанавливая его до одновалентной формы. Резкие концы титрования получены в случае обоих титрований, которые проводили в области температур  $50-95^\circ$ . Метод обладает замечательной точностью и воспроизводимостью.

**Microdosage du carbone dans les composés organiques par combustion quasi-instantanée et titrage coulométrique automatique du dioxyde de carbone:** D. FRAISSE, *Talanta*, 1971, **18**, 1011. (Service Central de Microanalyse du Centre National de la Recherche Scientifique, 2, rue Henry Dunant, 94-Thiais, France.)

**Summary**—A rapid simple method is described for the determination of carbon in organic compounds. The technique is based on a flash-combustion of the weighed sample (1–3 mg) in a hot empty combustion chamber at 950–1050° and swept by a stream of oxygen at a rate of 80–100 ml/min. Together with this flash and dynamic combustion in oxygen, a cupric oxide filling at 850° is necessary. Halogens and sulphur oxidation products are retained by means of a silvered alumina filling at 750–800°. Water and acidic oxides of nitrogen are absorbed at room temperature by means of magnesium perchlorate and manganese dioxide respectively. Carbon dioxide is absorbed in the cathodic compartment of an automatic coulometer and generates H<sup>+</sup> ions which are neutralized by OH<sup>-</sup> obtained by electrolysis. This method makes possible the determination of carbon in compounds containing halogens (including fluorine), phosphorus and metals. However, some metal compounds with polynuclear rings in their molecules give low results and require the addition of an oxidant to the sample in the boat for complete combustion. Vanadium pentoxide seems to be the best oxidant in the present working conditions. Solid samples are weighed and analysed in platinum or porcelain boats; liquid samples are weighed in Pyrex capillaries which are laid in platinum boats and covered with a small piece of platinum gauze. When normal liquid samples are analysed, one tip of the capillary is broken before its introduction into the combustion tube but in the case of volatile liquid samples the sealed capillary is introduced into the combustion chamber, where it explodes. The precision obtained is better than that of the classical methods.

**Photometric complex-formation titration of submicromole amounts of metal—II. The presence of other metals:** J. KRAGTEN, *Talanta*, 1971, **18**, 1023. (Natuurkundig Laboratorium, University of Amsterdam, The Netherlands.)

**Summary**—End-point extrapolation with the aid of a tangent to the spectrophotometric titration curve has been discussed theoretically for the metal-indicator complex MI with a ligand L in the presence of two other metals (P<sub>1</sub> and P<sub>2</sub>). It was found that a titration end-point can only be determined when the reaction of P<sub>1</sub> and P<sub>2</sub> with L takes place only negligibly during the titration of M. Two cases of practical interest can be distinguished. The metals may react either before or after the titration has been completed. For both situations titration conditions have been derived. With these titration conditions suitable experimental conditions can directly be derived from diagrams which were introduced in a previous paper. The theory developed has been applied to mixtures of manganese and magnesium but is generally applicable.

МИКРООПРЕДЕЛЕНИЕ УГЛЕРОДА В ОРГАНИЧЕСКИХ  
СОЕДИНЕНИЯХ КВАЗИМГНОВЕННЫМ  
СЖИГАНИЕМ И АВТОМАТИЧЕСКИМ  
КУЛОНОМЕТРИЧЕСКИМ ТИТРОВАНИЕМ  
ДВУОКИСИ УГЛЕРОДА:

D. FRAISSE, *Talanta*, 1971, **18**, 1011.

**Резюме**—Описан быстрый и несложный метод определения углерода в органических соединениях. Метод основан на квазимгновенном сжигании взвешенной пробы (1–3 мг) в камере горения при 950–1050°C в струе кислорода с скоростью 80–100 мл/мин. Вместе с этим квазимгновенным и динамическим сжиганием в кислороде надо использовать слой окиси меди при 850°C. Галогены и продукты окисления серы удерживаются на слое посеребренной окиси алюминия при 750–800°. Воду и кислые окиси азота поглощают при комнатной температуре перхлоратом магния и двуокисью марганца, соответственно. Двуокись углерода поглощается в катодном пространстве автоматического кулонометра и производит ионы  $H^+$  которые нейтрализуются электрогенерируемыми ионами  $OH^-$ . Этот метод позволяет определять углерод в соединениях содержащих галогены (включая фтор), фосфор и металлы. Между тем, некоторые металлоорганические соединения, содержащие в молекуле многоядерные кольца дают низкие результаты и изыскивают добавление окислителя пробы в лодочке, для получения совершенного сгорания. Пятиокись ванадия кажется самым лучшим окислителем в сегодняшних условиях. Твёрдые пробы взвешивают и анализируют в платиновых или фарфоровых лодочках; жидкие пробы взвешивают в капиллярах из стекла пайрекс, помещенных в платинов лодочках и покрытых небольшим куском платиновой сетки. В случае анализа нормальных жидких проб разбивают один край капилляра перед помещением в трубку для сжигания, но в случае летучих жидких проб запаянный капилляр помещают в трубку для сжигания, где он взрывается. Получаемая этим методом воспроизводимость лучше чем классических методов.

ФОТОМЕТРИЧЕСКОЕ КОМПЛЕКСООБРАЗУЮЩЕЕ  
ТИТРОВАНИЕ СУБМИКРОМОЛЕВЫХ КОЛИЧЕСТВ  
МЕТАЛЛОВ—II. ПРИСУТСТВИЕ ДРУГИХ  
МЕТАЛЛОВ:

J. KRAGTEN, *Talanta*, 1971, **18**, 1023.

**Резюме**—Обсуждена теоретически экстраполяция конца титрования с помощью тангенты на кривую спектрофотометрического титрования для случая комплекса металла-индикатора  $M_I$  с лигандом  $L$  в присутствии двух других металлов ( $P_1$  и  $P_2$ ). Найдено что концы титрования можно определять только когда в течение титрования  $M$  реакция  $P_1$  и  $P_2$  с  $L$  происходит только в незначительной мере. Можно различать два случая имеющие практический интерес. Металлы могут реагировать либо перед либо после законченного титрования. Разработаны условия титрования для обоих случаев. На основе этих условий титрования можно получать оптимальные опытные условия непосредственно из графиков приказанных в опубликованной ранее статье. Разработанная теория применена на смеси марганца и магния но она общеприменима.

**Statistical choice of standard samples and precision of analysis in emission spectroscopy:** ALLAN DANIELSSON, KURT JOHANSSON, FOLKE INGMAN and ROLF SUNDBERG, *Talanta*, 1971, **18**, 1033. (The Geological Survey of Sweden; Department of Analytical Chemistry, Royal Institute of Technology, Stockholm; and Statistical Research Group, University of Stockholm.)

**Summary**—An approach utilizing mathematical statistics to aid the choice of standard concentrations in emission spectroscopy is presented. The method is applied to the analysis of isoformed samples by the tape method. Some other possible applications (*e.g.* X-ray fluorescence, absorption photometry) are briefly discussed.

**AAS-Bestimmung von Natrium und Kalium in den hochschmelzenden Metallen Wolfram und Molybdän:** G. M. NEUMANN, *Talanta*, 1971, **18**, 1047. (Osram-Studiengesellschaft, München, B.R.D.)

**Summary**—Results for the atomic-absorption behaviour of sodium and potassium in the presence of large amounts of tungsten and molybdenum are reported. The mutual interference of the alkali metals is overcome by the addition of caesium. Of the matrix-elements tungsten showed no interference, while molybdenum had a proportional interference effect, which can be overcome by keeping the specimen weight at a constant value. Thus, AAS can be applied for the determination of K and Na in W and Mo without prior separation procedures. The sensitivity found for 1% absorption was 0.05  $\mu\text{g}$  of alkali/ml of solution.

**New methods for the detection of carboxylic acid groups in organic compounds, with acriflavine:** G. S. JOHAR, UMESH AGARWALA and H. S. SODHI, *Talanta*, 1971, **18**, 1051. (Department of Chemistry, V.S.S.D. College, Kanpur, India, and Department of Chemistry, D.A.V. College, Kanpur, India.)

**Summary**—The dye acriflavine is used for the selective detection of the carboxylic acid group in organic compounds. Two simple, rapid, and reliable colour tests are reported; these are based on the development of a violet colour and a yellow to yellowish-brown precipitate when a carboxylic acid is treated with acriflavine/sodium nitrite and acriflavine/potassium chromate respectively. Other acidic compounds such as phenols, thiophenols, sulphinic acids, sulphonamides, and acid imides do not interfere. Sulphonic acids (with the exception of their amino derivatives) interfere with both the tests. Enols and salts of organic bases do not interfere in the former test, whereas they do interfere in the latter test. The probable nature of the reaction products in both the tests has been discussed. Based on the former reaction, a procedure is described for the selective detection of nitrite ion. The limit of detection is 25  $\mu\text{g}$  of nitrite per ml. Only iodide interferes.

**Zur Verbesserung der Reproduzierbarkeit der Meßwerte bei photometrischen Bestimmungsverfahren:** S. KOCH and G. ACKERMANN, *Talanta*, 1971, **18**, 1055. (Bergakademie Freiberg, Lehrstuhl für Analytische Chemie, 92 Freiberg/Sachs., Leipziger Straße, D.D.R.)

**Summary**—The addition of a weak complexing agent to control interfering side-reactions is shown to increase the precision of the photometric determination of iron(III) with thiocyanate and of titanium(IV) with Tiron or with chromotropic acid.

СТАТИСТИЧЕСКИЙ ВЫБОР СТАНДАРТНЫХ  
ОБРАЗЦОВ И ВОСПРОИЗВОДИМОСТЬ АНАЛИЗА  
МЕТОДОМ ЭМИССИОННОЙ СПЕКТРОСКОПИИ:

ALLAN DANIELSSON, KURT JOHANSSON, FOLKE INGMAN and ROLF  
SUNDBERG, *Talanta*, 1971, **18**, 1033.

**Резюме**—Приведен подход применения математической статистики для выбора стандартных концентраций в анализе методом эмиссионной спектроскопии. Метод применен в анализе изоформированных проб методом ленты. Кратко обсуждены другие возможности применения метода (на пример в рентгеновской флуоресценции и абсорбционной фотометрии).

ОПРЕДЕЛЕНИЕ НАТРИЯ И КАЛИЯ В  
ВЫСОКОПЛАВКИХ МЕТАЛЛАХ ВОЛЬФРАМЕ И  
МОЛИБДЕНЕ МЕТОДОМ АТОМНО-  
АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

G. M. NEUMANN, *Talanta*, 1971, **18**, 1047.

**Резюме**—Приведены атомно-абсорбционные характеристики натрия и калия в присутствии больших количеств вольфрама и молибдена. Взаимодействие щелочных металлов избегнуто добавлением цезия. Среди матричных элементов вольфрам не показал мешающего действия, но молибден показал пропорциональный эффект, который можно избежать поддерживая постоянным вес пробы. Этим образом методом атомно-абсорбционной спектроскопии можно пользоваться для определения K и Na в вольфраме и молибдене без предварительного разделения. Чувствительность метода при 1% абсорбции составляет 0,05 мкг щелочи/мл раствора.

НОВЫЕ МЕТОДЫ ОБНАРУЖЕНИЯ  
КАРБОКСИЛЬНОЙ КИСЛОТНОЙ ГРУППЫ В  
ОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ С ИСПОЛЬЗОВАНИЕМ  
АКРИФЛАВИНА:

G. S. JONAR, UMESH AGARWALA and H. S. SODHI, *Talanta*, 1971, **18**, 1051.

**Резюме**—Краситель акрифлавин использован для селективного обнаружения карбоксильной кислотной группы в органических соединениях. Приведены два несложных, быстрых и надежных метода определения цвета; они основаны на проявлении фиолетовой окраски и желтого до желто-коричневого осадка при обработке карбоновой кислоты акрифлавином-нитритом натрия или акрифлавином-хроматом калия, соответственно. Другие кислые соединения как на пример фенолы, тиофенолы, сульфоновые кислоты, сульфонамиды и амиды кислот не мешают определению. Сульфоновые кислоты (за исключением их аминокислотных) влияют на оба метода. Энолы и соли органических оснований не мешают первому определению но мешают другому. Обсуждена природа продуктов реакций в случае обоих методов. Описана процедура для селективного определения нитритиола основанная на первой реакции. Чувствительность составляет 25 мкг нитрита на мл. Только подидион мешает определению.

УЛУЧШЕНИЕ ВОСПРОИЗВОДИМОСТИ  
ИЗМЕРЕНИЙ В СПЕКТРОФОТОМЕТРИЧЕСКИХ  
МЕТОДАХ АНАЛИЗА:

S. KOCH and G. ASKERMAN, *Talanta*, 1971, **18**, 1055.

**Резюме**—Показано что добавка слабого комплексообразующего агента с целью предотвращать мешающие боковые реакции повышает воспроизводимость спектрофотометрического определения железа(III) тиоцианатом и титана (IV) тироном или хромотроповой кислотой.

**Determination of arsenic and selenium in steel by an X-ray technique utilizing chemical preconcentration:** G. L. VASSILAROS, *Talanta*, 1971, **18**, 1057. (Colt Industries Crucible Inc., Materials Research Center, P.O. Box 88, Pittsburgh, Pennsylvania 15230, U.S.A.)

**Summary**—A chemical X-ray method is proposed for determining trace amounts of arsenic and selenium in steel. The method utilizes a prechemical separation from the iron matrix and concentration of arsenic and selenium on a micropore membrane by reduction to the free metal by tin(II). Selenium was found to be a suitable carrier for arsenic (300  $\mu\text{g}$  of selenium for the quantitative precipitation of 10–200  $\mu\text{g}$  of arsenic). Arsenic (300  $\mu\text{g}$ ) was found to be a suitable carrier for up to 200  $\mu\text{g}$  of selenium. Up to 200  $\mu\text{g}$  of tellurium and antimony were experimentally found not to be co-precipitated with either arsenic or selenium.

**Potassium thiocarbonate as a precipitant for platinum metals:** N. K. KAUSHIK and K. N. JOHRI, *Talanta*, 1971, **18**, 1061. (Department of Chemistry, University of Delhi, Delhi-7, India.)

**Summary**—Potassium thiocarbonate reagent is proposed for the gravimetric determination of ruthenium(III), rhodium(III), palladium(II) and platinum(IV) in a highly acidic medium (pH 0.5–0.7) under suitable conditions. Ni, Zn, Mn(II), Al, Fe(III), Ti(IV), Zr, Th, Ca, Ba, Sr and Mg do not interfere. The largest relative error is 0.7% and the average error 0.2%.

**Amperometric complex-formation titration of traces of thorium:** F. FREESE, R. OOSTERVINK and G. DEN BOEF, *Talanta*, 1971, **18**, 1064. (Laboratorium voor Analytische Scheikunde der Universiteit van Amsterdam, Nieuwe Achtergracht 125, Amsterdam-C, The Netherlands.)

**Summary**—Thorium has been determined in the microgram range by complexometric titration with EDTA. The end-point was detected by following the anodic wave of EDTA at a rotating mercury electrode. It has been shown that thorium can be titrated in the presence of large amounts of other metals. Following electrolysis at a mercury pool electrode the titration is selective for thorium.

**Determination of boron and nitrogen in boron nitride:** SANFORD L. ERICKSON and FRANK J. CONRAD, *Talanta*, 1971, **18**, 1066. (Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.)

**Summary**—Improved techniques are described for the determination of boron and nitrogen in pure boron nitride. Controlled fusion of boron nitride with sodium carbonate in a muffle furnace is followed by a potentiometric titration of the boric acid. A special quartz vessel is described for the determination of nitrogen. The boron nitride is fused with sodium hydroxide and the resulting ammonia is swept into a receiver and titrated with standard hydrochloric acid. Boron and nitrogen values with their standard deviation are given for a typical pure boron nitride.

ОПРЕДЕЛЕНИЕ МЫШЬЯКА И СЕЛЕНА В СТАЛИ  
МЕТОДОМ РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНЦИИ С  
ИСПОЛЬЗОВАНИЕМ ХИМИЧЕСКОЙ ПРЕКОНЦЕНТ-  
РАЦИИ:

G. L. VASSILAROS, *Talanta*, 1971, **18**, 1057.

**Резюме**—Предложен химическо-рентгеновский метод определения следовых количеств мышьяка и селена в стали. Метод пользуется предварительным химическим отделением элементов от матрицы железа и концентрированием мышьяка на микропористой мембране, восстановлением до металла оловом(II). Селен оказался подходящим носителем для мышьяка (300 мкг селена для количественного осаждения 10–200 мкг мышьяка). Мышьяк (300 мкг) оказался подходящим носителем для вплоть 200 мкг селена. Установлено опытом что вплоть 200 мкг теллура и сурьмы не соосаждаются ни мышьяком ни селеном.

ТИОКАРБОНАТ КАЛИЯ В КАЧЕСТВЕ  
ОСАДИТЕЛЯ ДЛЯ ПЛАТИНОВЫХ МЕТАЛЛОВ:

N. K. KAUSHIK and K. N. JONHI, *Talanta*, 1971, **18**, 1061.

**Резюме**—Тиокарбонат калия предложен в качестве осадителя для весового определения рутения(III), родия(III), палладия(II) и платины(IV) в сильноокислой среде (pH 0,5–0,7) в подходящих условиях. Ni, Zn, Mn(II), Al, Fe(III), Ti(IV), Zr, Th, Ca, Ba, Sr, и Mg не мешают определению. Самая большая относительная ошибка составляет 0,7%, а средняя ошибка—0,2%.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ СЛЕДОВ  
ТОРИЯ НА ОСНОВЕ КОМПЛЕКСООБРАЗОВАНИЯ:

F. FREESE, R. OOSTERVINK and G. DEN BOEF, *Talanta*, 1971, **18**, 1064.

**Резюме**—Микрограммовые количества тория определены комплексометрическим титрованием с ЭДТА. Конец титрования обнаружен прослеживанием анодной волны ЭДТА на вращающемся ртутном электроде. Показано что торий удается титровать в присутствии больших количеств других металлов. После электролиза с использованием ртутного электрода титрация является селективной для тория.

ОПРЕДЕЛЕНИЕ БОРА И АЗОТА В НИТРИДЕ  
БОРА:

SANFORD L. ERICKSON and FRANK J. CONRAD, *Talanta*, 1971, **18**, 1066.

**Резюме**—Описаны улучшенные методы определения бора и азота в чистом нитриде бора. Методы основаны на контролируемом плавлении нитрида бора с карбонатом натрия в муфельной печи, с последующим потенциометрическим титрованием борной кислоты. Описан специальный кварцевый сосуд для определения азота. Нитрид бора плавил с гидроокисью натрия, образованный аммиак собирали в приёмном сосуде и титровали с титрованным раствором соляной кислоты. Приведены значения определены для бора и азота в типическом чистом нитриде бора, вместе с стандартными ошибками.

**An improved colorimetric determination of vanadium in geochemical prospecting samples:** J. L. ROBERTS, *Talanta*, 1971, **18**, 1070. (Institute of Geological Sciences, Geochemical Division, 64-78, Gray's Inn Road, London, WC1X 8NG.)

**Summary**—The colorimetric method employed by the U.S. Geological Survey for the determination of vanadium in large numbers of geochemical prospecting samples has been examined. Use of sodium hydrogen sulphate for fusing the samples avoids precipitation of potassium phosphotungstate during colour development. Sensitivity and selectivity of the method are enhanced by extracting the phosphotungstovanadic acid into isobutyl methyl ketone.

**Rapid dissolution of sulphide ore for the determination of copper:** WILLIAM C. HOYLE and HARVEY DIEHL, *Talanta*, 1971, **18**, 1072. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

**Summary**—A mixture of equal volumes of perchloric acid and phosphoric acid is an excellent solvent for sulphide ores preliminary to the determination of copper. The dissolution is rapid, no bumping occurs, and the visual adjustment of pH prior to the iodometric determination of copper is easier.

**Determination of 0.01–0.1% of samarium in 40–100 mg of lead chloride:** J. AGTERDENBOS, B. A. H. G. JÜTTE and J. SCHURING, *Talanta*, 1971, **18**, 1074. (Analytisch Chemisch Laboratorium der Rijksuniversiteit Utrecht, Croesestraat 77A, Utrecht, The Netherlands.)

**Summary**—A method is described for the determination of 5–25  $\mu\text{g}$  of samarium in about 40 mg of lead chloride, based on the removal of the lead by electrolysis and determination of the samarium by extraction with PAN and measurement of the extinction of the complex at 552 nm.

**Synergistic effects in the solvent extraction of zinc with salicylaldoxime:** A. P. RAO and S. P. DUBEY, *Talanta*, 1971, **18**, 1076. (Chemistry Department, Indian Institute of Technology, Hauz Khas, New Delhi-29, India.)

**Summary**—The extraction of zinc with salicylaldoxime was studied. The adduct-forming tendency of zinc salicylaldoximate with pyridine,  $\alpha$ -picoline,  $\beta$ -picoline, quinoline and isoquinoline was also investigated. This tendency decreases in the order  $\beta$ -picoline > pyridine >  $\alpha$ -picoline > isoquinoline > quinoline.

**Dehydroacetic acid as a reagent for the separation and gravimetric determination of copper(II), aluminium and beryllium:** GURCHARAN SINGH MANKU and PRABHU DAYAL SARPAL, *Talanta*, 1971, **18**, 1079. (Department of Chemistry, Hans Raj College, Delhi-7, India.)

**Summary**—Dehydroacetic acid is proposed as a reagent for the gravimetric determination of copper(II), aluminium and beryllium at pH 3.0–6.0, 3.0–6.0 and 7.5–9.5 respectively. Copper is weighed as the complex  $\text{Cu}(\text{C}_8\text{H}_7\text{O}_4)_2$ . Aluminium and beryllium are weighed as  $\text{Al}_2\text{O}_3$  and  $\text{BeO}$ . The reagent is easy to prepare.



УЛУЧШЕННЫЙ МЕТОД КОЛОРИМЕТРИЧЕСКОГО  
ОПРЕДЕЛЕНИЯ ВАНАДИЯ В ОБРАЗЦАХ  
ГЕОХИМИЧЕСКОЙ РАЗВЕДКИ:

J. L. ROBERTS, *Talanta*, 1971, **18**, 1070.

**Резюме**—Испытан колориметрический метод, примененный инспекторами в определении ванадия в большом числе образцов геохимической разведки. Использование бисульфата натрия для плавления образца избегнуто осаждение фосфатовольфрамата калия при проявлении цвета. Чувствительность и селективность метода повышены экстрагированием фосфорно-ванадодвольфрамовой кислоты изобутилметилкетонном.

БЫСТРОЕ РАСТВОРЕНИЕ СУЛЬФИДНОЙ РУДЫ  
ДЛЯ ОПРЕДЕЛЕНИЯ МЕДИ:

WILLIAM C. HOYLE and HARVEY DIENL, *Talanta*, 1971, **18**, 1072.

**Резюме**—Смесь одинаковых объемов хлорной и фосфорной кислот является отличным растворителем для сульфидных руд в определении меди. Растворение поступает быстро без кипения с толчками, а визуальная установка pH прежде иодометрического титрования меди легче.

ОПРЕДЕЛЕНИЕ 0,01–0,1% САМАРИЯ В 40–100 МГ  
ХЛОРИДА СВИНЦА:

J. AGTERDENBOS, B. A. H. G. JÜTTE and J. SCHURING, *Talanta*, 1971, **18**, 1074.

**Резюме**—Описан метод определения 5–25 мкг самария в 40 мг хлорида свинца, основанный на устранении свинца путем электролиза и определении самария извлечением с ЦАН и измерением светопоглощения комплекса при 552 нм.

СИНЭРГЕТИЧЕСКИЕ ЭФФЕКТЫ ПРИ  
ИЗВЛЕЧЕНИИ ЦИНКА САЛИЦИЛАЛЬДОКСИМОМ:

A. P. RAO and S. P. DUBEY, *Talanta* 1971, **18**, 1076.

**Резюме**—Изучено извлечение цинка салицилальдоксимом. Также исследована тенденция образования салицилальдоксимата цинка с пиридином,  $\alpha$ -пиколином,  $\beta$ -пиколином, хинолином и изохинолином. Эта тенденция уменьшается в порядке  $\beta$ -пиколин > пиридин >  $\alpha$ -пиколин > изохинолин > хинолин.

ДЕГИДРАЦЕТОВАЯ КИСЛОТА В КАЧЕСТВЕ  
РЕАГЕНТА ДЛЯ ОТДЕЛЕНИЯ И ВЕСОВОГО  
ОПРЕДЕЛЕНИЯ МЕДИ(II), АЛЮМИНИЯ И  
БЕРИЛЛИЯ:

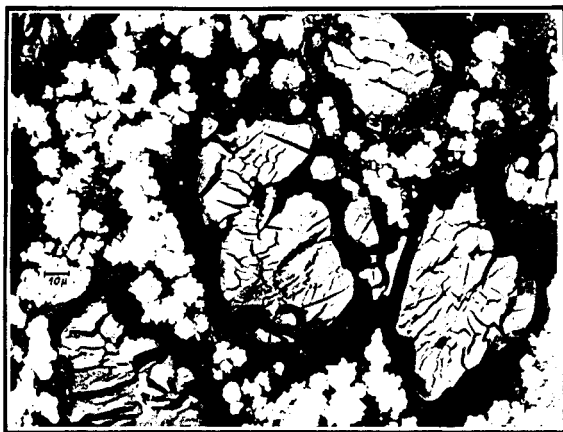
GURCHARAN SINGH MANKU and PRAVHU DAYAL SARPAL, *Talanta*, 1971, **18**, 1079.

**Резюме**—Дегидрацетовая кислота предложена в качестве реагента для весового определения меди(II), алюминия и бериллия при pH 3,0–6,0, 3,0–6,0 и 7,5–9,5, соответственно. Мед взвешивают в форме комплекса  $\text{Cu}(\text{C}_8\text{H}_7\text{O}_4)_2$ . Алюминий и бериллий взвешивают в форме  $\text{Al}_2\text{O}_3$  и  $\text{BeO}$ . Приготовление реагента несложно.

# ELECTROCHIMICA *Acta*

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Microphotograph of a DSK working layer.

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