ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

Editors

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ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 57, No. 1, 1–236, November 1971
Published monthly

Publication Schedule for 1971

In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1971. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

Vol. **53**, No. **1**	January 1971	
Vol. **53**, No. **2**	February 1971	**(completing Vol. 53)**
Vol. **54**, No. **1**	March 1971	
Vol. **54**, No. **2**	April 1971	
Vol. **54**, No. **3**	May 1971	**(completing Vol. 54)**
Vol. **55**, No. **1**	June 1971	
Vol. **55**, No. **2**	July 1971	**(completing Vol. 55)**
Vol. **56**, No. **1**	August 1971	
Vol. **56**, No. **2**	September 1971	
Vol. **56**, No. **3**	October 1971	**(completing Vol. 56)**
Vol. **57**, No. **1**	November 1971	
Vol. **57**, No. **2**	December 1971	**(completing Vol. 57)**

Subscription price: $17.50 or Dfl. 63.— per volume plus postage. Total subscription price for 1971: $87.50 or Dfl. 315.— plus postage. Additional cost for copies by airmail available on request. For subscribers in the U.S.A. and Canada, 2nd class postage paid at New York, N.Y. For advertising rates apply to the publishers.

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY P.O. Box 211, Amsterdam, The Netherlands

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Languages

Papers will be published in English, French or German.

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Oxonium Ions in Organic Chemistry

Although the alkylating action of trialkyloxonium salts has been known ever since their discovery in 1937, the general use of these powerful alkylating agents in organic syntheses found only gradual acceptance. The reason is probably to be sought in the prejudices of many preparative organic chemists who regarded the synthesis of these compounds as too involved and considered them rather difficult to handle. The past decade, however, has seen a great upsurge of preparative interest in trialkyloxonium salts. A second class of oxonium salts, dialkoxycarbonium salts, has recently also come to the fore as alkylating agents of general utility. Even the scope of the oldest class of tertiary oxonium salts, the pyrylium salts, is by no means exhausted, as was recently so clearly demonstrated by the synthesis of phosphabenzene derivatives from pyrylium salts.

Where as previous reviews were just concerned with particular aspects of oxonium salts – and primarily with pyrylium salts – the present work surveys the entire field of organic oxonium ions. Not only are the isolable tertiary oxonium salts – alkoxycarbonium, dialkoxycarbonium, trialkyloxonium, and pyrylium salts – considered but a detailed account is also given of primary and secondary oxonium ions which are often encountered only in solution. In addition to preparations, reactions, and preparative applications, a whole chapter is devoted to the occurrence of tertiary oxonium ions as intermediates in organic reactions.

1971. IX. 202 pages with 6 figures and 12 tables. Cloth DM 55,–.
ISBN: 3-527-25348-3 LC Catalog Card No.: 77-159512.
Published jointly with Academic Press, New York and London.

VERLAG CHEMIE · GMBH · WEINHEIM/BERGSTR.
ACADEMIC PRESS · NEW YORK AND LONDON

411G

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Vol. 57 (1971)

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AMSTERDAM

Anal. Chim. Acta, Vol. 57 (1971)

PRINTED IN THE NETHERLANDS

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DESIGN AND OPERATION OF A PHOTON-COUNTING SYSTEM FOR ANALYTICAL ATOMIC SPECTROMETRY

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(Received 25th May 1971)

Photon counting involves the digital measurement of the current pulses resulting at the anode of a photomultiplier caused by photon impact at the photocathode. Provided that the rate of photo-electron emission and the frequency response of the measurement system are such that individual current pulses are resolved, then the measurement affords a direct digital analysis of the intensity of radiation falling on the photomultiplier. At present, the most practical means for photon counting is the photomultiplier and hence any analytical technique which relies on the measurement of a radiation intensity in the ultraviolet–visible region of the electromagnetic spectrum is amenable to photon counting. The fundamentals of the photon-counting method have been reviewed recently by Morton[1] and some of the basic practical considerations for application in solution absorption spectrophotometry have been described by Malmstadt *et al.*[2] and Piepmeier *et al.*[3]. However, photon counting is best suited to the measurement of low levels of radiation and hence its application in analytical atomic absorption, emission and fluorescence spectrometry is obvious, although it has not previously been described for such purposes. This is perhaps not surprising in one respect because the instrumentation associated with atomic spectrometry imposes considerably more restrictions on the detector system than most other analytical techniques. On the other hand, the current trend in atomic spectrometry towards the use of non-flame atom reservoirs requires that close attention must be given to the response characteristics of the detector system used. Many non-flame devices frequently produce weak transient signals at the detector and conventional d.c. level measurements (*e.g.* with potentiometric recorders), designed primarily for steady state measurements are in consequence often unsatisfactory. The use of high-speed recorders is possible in certain instances provided that the response time of the various electronic components present in the experimental system is comparable with, or preferably less than, that of the signal duration[4]. The most obvious method of measurement in such instances is integration, which apart from the work of L'Vov[5], has received little attention in atomic spectrometry. Photon counting is ideally suited to such studies, and gives precise direct digital presentation of the weak transient signals produced. Further advantages of photon counting are the elimination of the reading error and the ability to increase the signal: noise ratio by pulse-height discrimination against unwanted anode voltage pulses. One disadvantage of photon counting concerns its reported inability to cope with relatively high background systems which would quickly result in pulse pile-up problems. However, the use of non-flame atom reservoirs in particular is not normally associated with a high radiative background and some preliminary experiments made in our laboratory[6] with photon counting in flame emission and fluorescence spectrometry indicate that this need not be a limitation with flames.

The purpose of this paper is to report the theory, design and operation of a simple photon-counting device which is suited to the measurement of radiation signals encountered in flame and non-flame atomic spectrometry. The general approach involves consideration of a typical experimental system used in atomic absorption, emission and fluorescence spectrometry and the development of a photon-counting system which can be linked to such a system without redesigning the basic experimental system and without the need for complex interfacing. In addition particular attention is given to the use of photon counting for integrating the transient-type signal commonly encountered with many non-flame cells.

BASIC CONSIDERATIONS

Photon arrival statistics

It is assumed that flame atom reservoirs, when used in atomic emission and fluorescence spectrometric analysis, give rise to emission of photons which are randomly distributed with respect to time. In such instances the photons can be regarded as random events occurring in a continuum, *i.e.* they are Poisson-distributed with mean λ and variance σ^2 where $\lambda = \sigma^2$ and $P(r) = e^{-\lambda}\lambda^r/r!$, $P(r)$ being the probability of r events occurring when the average rate of occurrence is λ. It follows that the intervals between photon arrivals will have a negative exponential distribution for which the probability density function is given by

$$f(t) = \lambda \exp^{-\lambda x}$$

where t is the time and x is the time interval.

In the light of these facts a computer programme was written simulating the arrival and count of a number of photons at a photomultiplier. Three variables were specified, namely

(*a*) the average rate of photon arrival (λ)
(*b*) the count period (T) and
(*c*) the counter "dead time" (D).

The dead time may be related to the ability of the detector system to resolve two closely spaced photons. If the first photon arrives after time, t, then the counter will not be able to respond to another photon until after the time, $t+D$, and any occurring within this interval will not be counted. If the next photon arrives after time, $t+D+x$ (where x is a further increment in time), then it will be counted, but no more will be counted until after time, $t+D+x+D$. For a given set of variables (λ, T and D) the programme predicts the total number of photon arrivals, P, the total number of photon arrivals not counted, N, and their frequency distribution. Information was thus obtained concerning the importance of the ratios $\lambda:D$ and $T:\lambda$.

Figure 1 shows the percentage of photons counted as a function of the arrival rate for a given dead time, D. Clearly, if the system is to be used as an absolute radiation measuring device with less than 1% error caused by loss, then the count rate should not exceed 0.01 times the reciprocal counter dead time. The frequency distribution of missed photons also depends on their count rate as shown in Fig. 2. The count period, T,

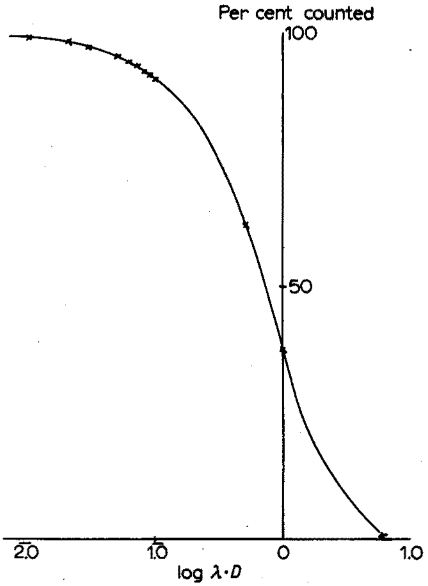

Fig. 1. Percentage of photons counted as a function of the arrival rate and counting system dead time.

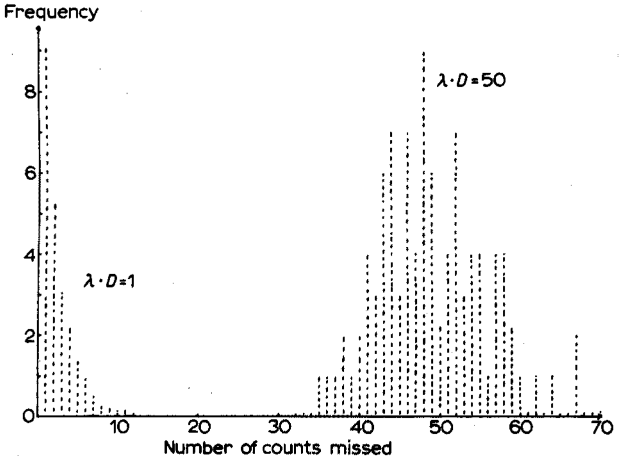

Fig. 2. Frequency distribution of missed photons as a function of count rate.

indicates the precision of counting and Fig. 3 shows for two count rates the count period required before the percentage of photons missed reaches a limit.

For large values of λ (*e.g.* 100), the Poisson distribution is closely approximated to the normal distribution; this will be the situation with the photon-counting studies described in this manuscript.

The conclusions established using the computer programme are based on an ideal system, but they should serve as an indication of a practical situation.

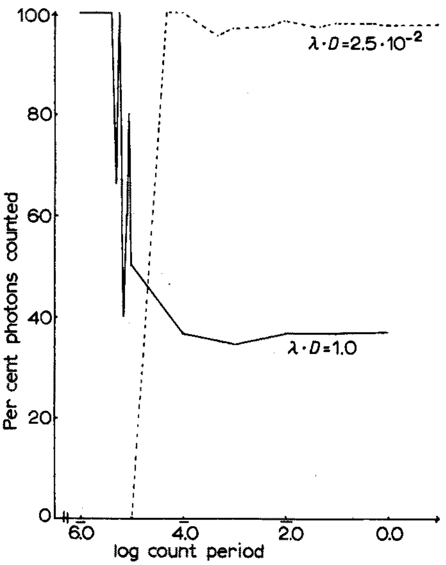

Fig. 3. The count period required before the percentage of missed photons reaches a limit.

The photomultiplier

At present the photomultiplier must be regarded as the most suitable device available for photon counting, although in the future it will undoubtedly be replaced by photoconductive devices. Photons falling on the photocathode cause the emission of photoelectrons with a probability, k, usually referred to as the quantum efficiency (k depends on the wavelength of the incident radiation and the work functions of the photocathode surface). The photoelectrons are then accelerated through a potential gradient onto the first dynode where each causes the emission of secondary electrons; the secondary emission coefficient $\bar{\delta}$, usually assumes values in the range 3–6. The multiplication process continues down the dynode chain so that the resultant output signal is a current pulse.

The magnitude of the charge packet from an ideal photomultiplier would be $\bar{\delta}^n e$ coulombs (where n is number of dynodes in chain). However, this does not take into account the fact that the cathode to first dynode collection efficiency (ε) is seldom greater than 90% with practical photomultipliers and the inter-dynode transfer efficiency (η) is not quite 100%. A better expression for the overall gain would be given by

$$G = \varepsilon(\eta\bar{\delta})^n \, .$$

Because these parameters are difficult to measure, most manufacturers express the photomultiplier gain as

$$G = \frac{M}{S} \cdot 10^6$$

where M is the overall photomultiplier sensitivity (A/lumen) and S is the cathode sensitivity (μA/lumen). In practice, the gain of the photomultiplier fluctuates because the secondary emission coefficient δ is a statistical quantity, $\bar{\delta}$ being its mean value. It follows that the variance of the multiplier gain is given by

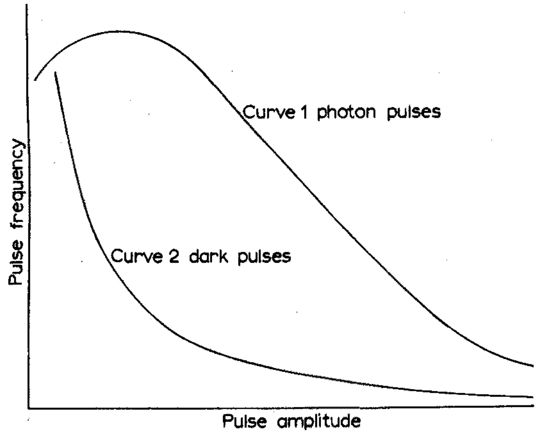

Fig. 4. Amplitude–frequency distributions for photoelectron and dark pulses from a photomultiplier.

$$(\sigma_G/\bar{G})^2 = 1/(\bar{\delta}-1)$$

Figure 4 (curve 1) shows the amplitude–frequency distribution for photoelectron pulses which results from the gain variation of the photomultiplier dynode chain.

The discussion so far has dealt only with the magnitude of the charge packet arriving at the anode and no mention has been made of its shape. If all the electrons traverse exactly the same path through the photomultiplier then they would arrive simultaneously at the anode producing an infinite current pulse. There is however, a variation in the electron paths between cathode and anode which causes a spread in their transit time (τ^1). The distribution of τ^1 depends on the dynode structure of the photomultiplier although Lewis and Wells[7] proposed that the normal distribution was a suitable approximation for the most commonly used configurations, *e.g.* box and grid and Venetian blind types. Thus, the time distribution of the anode current pulse for a single photon is given by

$$I(t) = Ge/\sigma(2\pi)^{\frac{1}{2}} \exp^{-t^2}/2\sigma^2$$

where σ is the standard deviation of the charge arrival rate about the mean, t is the time and e is the charge on the electron.

Photon counting is a noise-limited process, noise being defined as the random fluctuation occurring in the signal level. Constant background signals do not constitute noise because they may be measured with high precision and subtracted.

A photomultiplier when placed in complete darkness with the operating voltage applied will yield a small current typically between 0.1–15 nA depending on the photomultiplier type. This is the so-called dark current which arises from the following causes.

Thermionic emission from the photocathode. The electrons released by this process are indistinguishable from photoelectrons and therefore the statistical variation in their number is a serious source of noise at very low radiation levels. With most photocathodes this type of emission represents the largest component of dark current and is given by Richardson's law (in A):

$$I(t) = 1.20 \cdot 10^2\, AT^2 \exp(-1.16 \cdot 10^4 \phi_t/T)$$

where T is the absolute temperature in °K, A is the area of photocathode in cm^2 and ϕ_t is the thermal work function of the photocathode.

A reduction in $I(t)$ can be achieved therefore by cooling the photomultiplier ($I(t)$ is virtually eliminated at $-40°$) or by limiting the effective cathode area. Capped tubes are produced by most manufacturers with cathode diameters as small as 10 mm and further improvements are possible by suitable arrangements of the external optics. When very low dark currents are desired and cooling is mechanically difficult, as with many commercial spectrophotometers, specially processed photocathodes are available with higher than normal values of ϕ_t (*e.g.* E.M.I. S-type photomultipliers).

Thermionic emission also takes place from the dynode chain, but the pulse-height distribution in this instance is different from that of the photoelectrons because the amplification factor varies according to the dynode number (Fig. 4, curve 2). Exposing photomultipliers to day-light is not harmful (provided that EHT is not applied), but it does result in some energy being trapped in the cathode and before use the photomultiplier should be left in the dark for 24–48 h to allow this energy to dissipate and reduce the thermionic current component.

Pulses originating from radioactive sources. The glasses used in photomultiplier manufacture contain residual amounts of natural ^{40}K isotope, which may result in photon bursts, but the level of ^{40}K in quartz is fortunately low. Cosmic particles show the same effect and may also cause electron emission from the cathode and dynode chain. Finally, glass fluorescence may occur, if the tube is exposed to γ-radiation.

The amplitude of the photoelectron pulses originating from radioactive sources is normally high because the original photon pulse can occur in a time interval an order of magnitude or more below the minimum pulse width which can be obtained at the anode.

Cold field emission and residual gas ionisation. Pulses from these sources are not important when the photomultiplier is run at the recommended voltages, but they are the limiting dark current component at higher voltages.

Ohmic leakage. Small d.c. currents always exist in photomultipliers, possibly because of anode drift of electrons which are not collected by the dynode chain. However, these unpulsed currents do not contribute to the background level in photon counting.

It may also be mentioned that any metallic components touching the photomultiplier not at cathode potential and electrostatic and magnetic fields can affect the potential distribution within the photomultiplier causing considerable increases in the dark current. Shields (mu-metal) are available which help to protect the photomultiplier from external influences.

The difference between the amplitude spectra of the signal and noise pulses (although background does not constitute noise, it must be regarded as a time integral of it and therefore higher background levels will invariably be associated with higher noise) is of paramount importance in photon counting because it enables discrimination against noise pulses. The noise spectrum has proportionally more pulses at each end of the amplitude spectrum than the signal spectrum (see above). Ideally therefore, "window counting" should be used, *i.e.* counting only those pulses in a certain amplitude range[1]. In practical atomic spectrometry, however, the high amplitude noise pulses may represent a very small fraction of the total count so that the upper amplitude level is not important. The value of the lower amplitude level should be set so as to maximize the signal:noise ratio.

The dynode chain circuit

The prime function of this circuit, in conjunction with the EHT supply, is to maintain steady potential gradients along the cathode–dynode chain. Drift in the operating voltage causes drift in the photomultiplier gain which in turn alters the effective discrimination level.

Three dynode configurations are commonly used, *viz.* box and grid, Venetian blind and the fast focussed types. From the applied voltage and gain stability aspect, the Venetian blind types photomultipliers are best.

Photomultiplier anode circuit

The photomultiplier acts as an almost perfect current generator and therefore it is usual to use this current to develop a voltage across a load resistor R_L. In high-frequency applications the cathode–dynode to earth capacity (*ca.* 6 pF) plus the capacity of any coaxial leads used becomes important so that the net output circuit is a parallel CR network. The rise time of a pulse is defined as the time required for it to rise from 10 to 90% of its maximum value and its width is defined as the full width at half maximum height (FWHM) which for a Gaussian-shaped pulse is equal to 2.36σ. The maximum voltage that such a pulse can develop in the anode circuit is given by

$$V_{\max} = C_s^{-1}\ Ge/\sigma(2\pi)^{\frac{1}{2}} \int_{-\infty}^{\infty} \exp^{-t^2}/2\sigma^2 \,\mathrm{d}t$$

where C_s is the total stray capacity.

The maximum voltage is equal to Ge/C_s when the time constant $R_L C_s$ tends to infinity. Thus, when 2.36σ is short compared with $R_L C_s$, the pulse charges C_s and then the voltage decays exponentially with time constant $R_L C_s$. When $R_L C_s \ll 1/f$ (where f is the maximum anticipated pulse repetition frequency), then pulses will not pile up in C_s. Under this condition the pulse shape would be fairly well preserved throughout the network. However, when $R_L C_s \simeq \sigma$, the charging and discharging rates of the capacitor are similar and therefore the maximum voltage developed is considerably less (the "ballistic deficit").

Pulse pile-up involves two or more unresolved pulses. Noise, dark current and background pulses all contribute and adversely affect the situation predicted earlier for photon pile-up. There are two net effects when pulse pile-up occurs: *two* small pulses which should be rejected by the discriminator may lead to amplitude addition and hence be counted as *one* pulse, *i.e.* a net gain of one pulse; and *two* large unresolved pulses may be counted as *one* pulse, *i.e.* a net loss of one pulse.

It is clear that the choice of the value $R_L C_s$ must be a compromise between keeping the anode time constant short and limiting the photoelectron pile-up, and providing a voltage pulse of reasonable amplitude to the input of the amplifier. Because the maximum pulse repetition frequency is usually limited by the bandwidth of the amplification system, the latter consideration is given most weight. Consider the example of a photomultiplier with a gain of $4 \cdot 10^6$, a total stray capacity of 30 pF and a σ value of 20 nsec. The maximum output voltage ($V_{\max}$) from a single photon would be 21.3 mV (*i.e.* Ge/C_s). If the value of R_L was 2 kΩ, then the maximum pulse repetition frequency ($1/R_L C_s$) would be 16.7 MHz and the ratio $R_L C_s/\sigma$ is *ca.* 3. This gives a value of the "ballistic deficit" such that the maximum output voltage would be *ca.* 10 mV (from $V_{\max} = 21.3 \cdot 1.2/(2\pi)^{\frac{1}{2}}$).

Some random noise is generated within the amplifier system, but by ensuring that the input photoelectron pulse height is sufficiently large, then the resulting amplified pulses will be much larger than the noise pulses which may then be eliminated by discrimination.

The amplifier

A low-noise amplifier with good long-term gain stability should be chosen for photon counting. For a.c. amplifiers, a large bandwidth which is compatible with gain, noise and stability requirements should be sought. The advantage of a.c. amplifiers is that their low-frequency cut-off helps to limit flicker noise (inherent in transistors) and they are not subject to baseline shift provided that the duty cycle is kept low. This will automatically be low if the requirement for less than 1% loss of photons (see *Photon arrival statistics*) is met.

The pulse-height discriminator

Gain stability coupled with adequate frequency response and amplitude sensitivity is of prime importance. The larger the pulses resulting from the amplifier, then the less stringent are the demands on the discriminator. For example, if the output pulses are several volts in magnitude with a standard deviation of 1 V, a simple potentiometric divider is an adequate discriminator. However, if the pulses are of the order of millivolts with a standard deviation of about 1 mV, then a more sophisticated device is required, *e.g.* an operational amplifier employing positive feedback (Schmitt Trigger)[2]. Provided that a discriminator with a sufficient sensitivity and frequency response can be constructed, then the direct interfacing of this device with a very high-gain photomultiplier would obviate the need for an amplifier. Such a system would have a higher frequency range of operation and there might also be a cost saving.

There is a case for no discrimination, although this is not possible in the true sense of the word because most frequency meters have a sensitivity control which effectively acts as a discriminator. Probably the most worthwhile course of action is to reduce the extraneous sources of noise by cooling the photomultiplier and employ no pulse-height discrimination. It is therefore possible in theory to bypass the discriminator and amplifier in photon counting and no doubt such systems will be designed in the near future.

The frequency meter

Basically the frequency meter should have good frequency response and a sufficiently large register to cope with the large numbers involved in photon counting. Accurate timing of the count period is essential and frequency meters used in photon counting should not have a time error exceeding 0.1%. Sensitivity controls are provided on most instruments which can be used as pulse-height discriminators provided that they have sufficient amplitude resolution in the voltage pulse range. Frequency meters capable of simple arithmetic operation and possessing data printout facilities would probably be best for photon counting on a routine basis.

The detection limit

The variance of the Poisson distribution is equal to the mean, hence the random fluctuation of the count about the mean is equal to the square root of the mean, *i.e.* the standard deviation for a Gaussian distribution.

If N_s is the signal count rate, N_d the background count rate and T is the count period, then the standard deviation or noise in the total count is given by

$$(N_s + N_d)^{\frac{1}{2}} T^{\frac{1}{2}}$$

Hence the signal: noise ratio is

$$S/N = N_s T^{\frac{1}{2}}/(N_s + N_d)^{\frac{1}{2}}$$

However, as the background count rate has to be measured separately from the total count, a further error is introduced so that the ratio becomes

$$S/N = N_s T^{\frac{1}{2}}/(N_s + 2N_d)^{\frac{1}{2}}$$

The precision of measurement is the inverse of the signal:noise ratio, expressed as a percentage, and hence the value of long count periods becomes apparent. For example, a ten-fold increase in the count period improves the precision by a factor of $10^{\frac{1}{2}}$.

One definition of the detection limit is the minimum signal count which can be resolved above the background. However, this is not entirely compatible with expressing the detection limit as the value recorded when the signal:noise ratio is unity. When the detection limit is approached, $N_d \gg N_s$ so that the above equation becomes

$$S/N = N_s T^{\frac{1}{2}}/(2N_d)^{\frac{1}{2}}$$

For a Gaussian distribution having mean N_d and measured standard deviation $(2N_d)^{\frac{1}{2}}$, the percentage of times that the measured N_d might be expected to take a value of less than $N_d - (2N_d)^{\frac{1}{2}}$, is approximately 15.9. On these occasions N_s may not be detected at all. The independent fluctuation of N_s could slightly improve or worsen the situation, although the major error component arises from the background count. This seems to be unsatisfactory and it would be better to take the detection limit as the value recorded when the signal:noise ratio is equal to 2. Under these conditions the above percentage reduces to 2.3%.

EXPERIMENTAL

Apparatus

The radiation was viewed with a Unicam SP900 spectrophotometer fitted with an EMI 9601B photomultiplier (consisting of eleven dynodes of the box and grid type yielding a typical gain of $4 \cdot 10^6$). Photoelectron pulses from the photomultiplier were amplified by a wideband a.c. amplifier (AIM Electronics, Cambridge, U.K., type ACA 123 powered by module PSU 101). The amplifier has a variable gain (in 5 stages) from 1000, when the band width is 0.6–4.5 MHz, to 30 dB down, when the band width is 0.6–6 MHz. The amplified pulses were counted by a frequency meter (Venner Electronics, Kingston-on-Thames, Surrey, type TSA 6636/3) capable of 40-MHz operation and having a six digit read-out. The sensitivity control of the frequency meter served as an adequate discriminator. Correct matching of the various units is important because this limits the stray electrical noise and preserves the theoretical bandwidth.

Operation and evaluation of system

The photon-counting system was evaluated by plotting photon count *vs.* d.c.

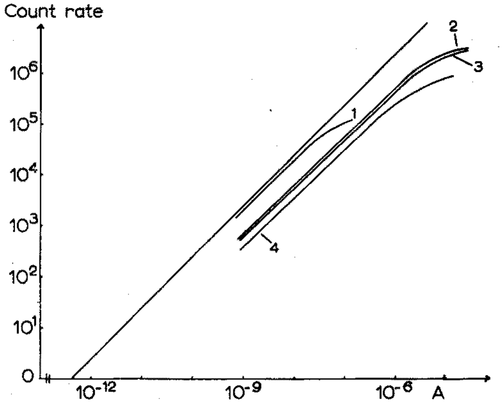

Fig. 5. Variation of photon count with d.c. current. (1) Obtained with EMI 9526B photomultiplier and effective load resistor 4.7 kΩ; (2) obtained with EMI 9601B photomultiplier and load resistor 450 Ω; (3) obtained with EMI 9601B photomultiplier and load resistor 470 Ω; (4) obtained with EMI 9601B photomultiplier and load resistor 1000 Ω. Theoretical curve for EMI 9526B photomultiplier.

current as shown in Fig. 5. For these measurements the monochromator slit was illuminated with a tungsten filament lamp and the wavelength selector was set at 550 nm. The output from the photomultiplier was connected directly to a Servoscribe potentiometric recorder with a 20 kΩ load resistor across the input terminals. The lamp voltage was adjusted so that with a slit width of 0.15 mm, about $5 \cdot 10^{-6}$ A was drawn from the photomultiplier. This procedure ensured that the radiation intensity falling on the photomultiplier cathode could be accurately adjusted with the slit-width control of the instrument. The slit-width was reduced then until the minimum measurable current from the photomultiplier was found. Beginning at this slit-width, and increasing in steps of 0.01 mm, the photomultiplier tube current was measured and the equivalent photon count rate was determined from periods of 4 and 10 sec. Readings were taken until it was clear that the count rate was no longer increasing in proportion to the current.

An oscilloscope was used to check that there was no shift of the amplified pulse base line from a.c. coupling. At a photomultiplier output of $3 \cdot 10^{-6}$ A, a shift of 5% was recorded which would not significantly alter the effective discrimination level. This current is approximately an order of magnitude higher than would normally be encountered in a typical photon-counting experiment. The theoretical count curve, derived by calculating the output current from the photomultiplier for a given number of photoelectrons released from the cathode (*i.e.* output current is equal to NGe where N is the number of photoelectrons released from the cathode per sec and Ge is the total gain multiplied by the charge on the electron) is shown in Fig. 5.

The curve indicating 80% of the theoretical count (curve 1) was obtained when the signal : noise was set at a maximum. The separation of the experimental and theoretical curves arises from the existence of d.c. currents within the photomultiplier, the variation in the electron pulse height and the pulse pile-up phenomenon. The magnitude of the separation can be regarded as a measure of the sensitivity of the system and the sensitivity may be decreased by raising the discriminator level.

The curvature at high photon counts is due to pulse pile-up and the effect on pulse pile-up of four different load resistors, ranging from 4.7 kΩ (the input impedance of the amplifier) to 50 Ω, is shown in Fig. 5, curves 1–4. The similarity in curves 2 and 3 suggests that the curvature is determined by the amplifier band width although curves 1 and 4 appear to be limited by the time constant of the photomultiplier circuit $R_L C_s$ (C_s was found to be *ca.* 40 pF). At the 4.5-MHz, 3-dB point of the amplifier, the curve for 50 Ω reached a value of 0.6 of the extrapolated straight line value, *i.e.* 2.7 MHz.

Further improvements in photon-counting systems depend on the design of low-noise, high-frequency electronics. For a system of given frequency response, the noise level must be reduced for optimal sensitivity; for a system with a given noise level the linear photon-counting range is determined mainly by the frequency response of the system. In terms of analytical procedures, these criteria can be equated with lower detection limits and longer linear working ranges, respectively.

Integration of transient radiation signals

The technique of signal integration is generally accepted as yielding the most sensitive and precise method of measuring analytical radiation signals. With the present tendency towards the use of non-flame atom reservoirs in atomic absorption and fluorescence spectrometry, signal integration assumes even greater importance, for the transient, weak signals produced cannot always be followed accurately by conventional d.c. systems. Also, if the signals have asymmetric and/or irreproducible profiles, rapid signal integration becomes essential. The photon-counting system described above provides rapid signal integration automatically and also gives a digital read-out which facilitates data handling processes.

Signal integration by photon counting was evaluated with a camera shutter to provide timed pulses of radiation from a tungsten filament bulb powered by a stabilised d.c. supply. The shutter speed was timed and checked for reproducibility with a storage oscilloscope. The results obtained by photon counting were compared with a d.c. amplifier–integrator system[8] (Table I). Although the photon-counting system showed only marginally better precision than the d.c. amplifier–integrator, it must be appreciated that the count period was considerably longer than the signal duration in these experiments. Furthermore, it was necessary to reset the recorder base-line level before each measurement with the d.c. amplifier–integrator and hence the use of photon counting is to be preferred in such circumstances.

The standard deviations in the above experiments were not derived from counting statistics because indiscriminate use of this method should be avoided un-

TABLE I

INTEGRATION OF TRANSIENT RADIATION SIGNALS

Shutter speed (msec)	*Photon counting*			*D.c. amplifier–integrator*		
	Average count[a] *(sec*$^{-1}$*)*	*Standard deviation*[a]	*Relative standard deviation* (%)	*Average signal*[b]	*Standard deviation*[a]	*Relative standard deviation* (%)
8.0±0.5	125.9	34.45	27.9	4.367	1.227	28.1
40.0±2.0	10781	225.1	2.09	40.31	0.9386	2.33

[a] Obtained from 30 repetitive counts. [b] Obtained from 30 repetitive readings.

TABLE II

COMPARISON OF STANDARD DEVIATIONS MEASURED EXPERIMENTALLY AND OBTAINED FROM COUNTING STATISTICS

Photon-counting system	*Average count* (sec^{-1})	*Standard deviation*[a]	
		Repetitive readings	*Counting statistics*
Typical dark count	468.7	20.33	21.63
Typical count from W lamp at 550.0 nm	26654	218.9	166.1
Typical count from microwave plasma[8] at 228.8 nm	81019	661.4	290.9

[a] Obtained from 30 repetitive counts.

less attention is given to the nature of the signal and the count period to avoid misinterpretation of results. Table II shows some typical photon counts and their standard deviations derived from repetitive readings and counting statistics. In each instance, except the first low dark count (468.7 sec^{-1}), a discrepancy exists between the two differently derived standard deviations. The larger experimental values arise from what could be termed the sampling error which is inherent in any practical system. This general term will encompass variations caused by (*a*) random fluctuations in the count period (these should be extremely small when the count period is derived from a crystal oscillator); (*b*) variations in the performance of the photon-counting system as a result of slight changes in the discriminator level, changes in the amplifier–photomultiplier gain, energy trapping in the photomultiplier cathode and possibly electrical pick up from other apparatus; and (*c*) random fluctuations in the intensity of the light source under observation, especially those of low frequency such as plasma and flame flicker, nebuliser surging, etc.

The results indicated, as expected, that source variation is usually the limiting factor in the precision of measurement. Thus when photon counting is used, the error involved in counting randomly distributed events is often outweighed by the "sampling error"; in these instances the normal statistical methods will yield more reliable results than those obtained from counting statistics. In both cases, increasing the count period, *i.e.* increasing the number of samples taken, improves the precision of measurement.

The photon counts obtained from the transient radiation measurements present a different problem because the signal is of finite duration. No device was available for synchronising the count period with the shutter operation and hence it was necessary to use a 1-sec count period (one of the counter gating times) for which the dark count was 468.7 and the standard deviation 20.33. If the background count is higher or equivalent to the signal count (*i.e.* at the detection limit) correct synchronization of the signal duration with the count period is essential. This can be demonstrated by calculating the signal:noise ratio for the 8-msec radiation pulses both from counting statistics and the normal experimental method; the two values being 3.86 and 3.65 respectively for a 1-sec count period. The background count for 8 msec would have been 3.75 counts, which together with the corresponding standard deviation, can be ignored. Recalculation of the signal:noise ratio based on an 8-msec count period yields values of 10.9 and 4.5 respectively (the signal variance in the second case being calculated by subtracting the background variance from the total measured variance). Optimal count timing appears therefore to increase the signal:noise ratio and it may well be that when dealing with signal profiles approximating to Gaussian distributions, then counting over the FWHM rather than the total signal width will yield the most favourable results.

Finally, the photon-counting system described above was used to detect transient emission signals at 228.8 nm arising from cadmium salts vapourised into a microwave-excited argon plasma by the platinum loop method[8]. The sampling size of the loop was 0.1 μl and the signal duration for a solution containing 0.01 μg Cd ml^{-1} was found to be *ca.* 350 msec. It was observed by means of photon counting that this time tended to increase slightly with concentration probably as a result of cadmium deposition on the walls of the plasma cell which was revapourised subsequently. A 1-sec count period was chosen which enabled the vapourisation process and count period to be manually synchronized without excessive error. The analytical curve obtained is shown in Fig. 6, and the limit of detection, based on a signal:noise ratio of 2, was $2 \cdot 10^{-13}$ g of cadmium, which is similar to that obtained in previous studies with a d.c. amplifier–integrator[8]. However, it must be appreciated that an unduly long count period was used in these photon-counting experiments, and that the spectrophotometer slit-width was 0.06 mm in comparison to 0.1 mm in the previous studies[8]. Hence it may be concluded that photon counting possesses the capability, when more

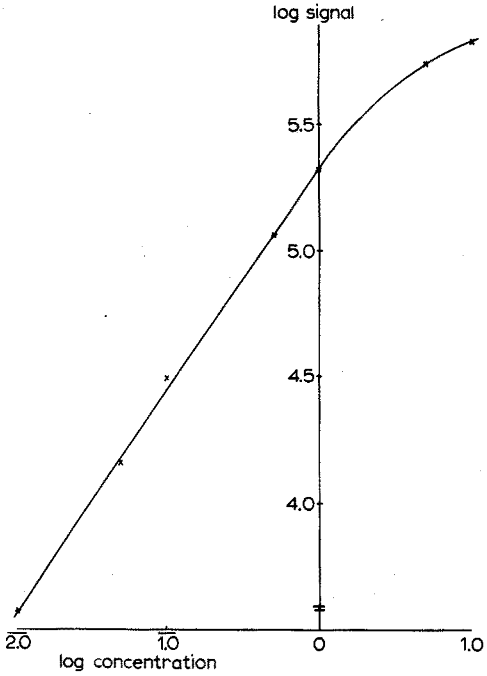

Fig. 6. Analytical working curve for cadmium.

completely optimized, of achieving lower limits of detection than conventional d.c. amplifier–integrator systems. The simplicity of the system and the ease of operation and interpretation of results should further encourage the use of photon counting in both steady state and transient spectrometric studies.

We would like to thank the Science Research Council for a studentship to one of us (B.L.S.) and for the provision of a research grant towards the purchase of some of the equipment used in this study.

SUMMARY

A simple photon-counting system is proposed for conventional flame and non-flame atomic spectrometric purposes. The current pulses from the photomultiplier are amplified by a wide band-width amplifier and fed directly to a frequency meter. Discrimination is provided by the sensitivity control of the frequency meter. The system is evaluated with respect to frequency response, linear working range and as a digital integrating device.

RÉSUMÉ

Un système de photon-comptage simple est proposé pour la spectrométrie atomique de flamme conventionnelle et la spectrométrie sans flamme. Les impulsions de courant du photomultiplicateur sont amplifieés et transmises directement à un fréquence-mètre. Réponse de fréquence, domaine de travail linéaire et appareil digital sont pris en considération.

ZUSAMMENFASSUNG

Es wird eine einfache Photonenzähleinrichtung für die konventionelle Flammen-Atomspektrometrie und die flammenlose Atomspektrometrie vorgeschlagen. Die Stromimpulse aus dem Photomultiplier werden mit einem Breitbandverstärker verstärkt und unmittelbar einem Frequenzmesser zugeführt. Eine Diskriminierung wird durch die Empfindlichkeitsregelung des Frequenzmessers erreicht. Das System wird im Hinblick auf Frequenzverhalten, linearen Arbeitsbereich und als Digitalintegriereinrichtung geprüft.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

PART V. DETERMINATION OF ELEMENTS IN ORGANIC SOLVENTS*

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(Received 15th March 1971)

The use of the carbon filament as an atom reservoir for aqueous samples in atomic absorption and fluorescence spectroscopy has been described in earlier parts of this series. If the carbon filament could be used to atomise elements from organic solvents, solvent extraction could be applied in separation and preconcentration procedures for this type of analysis. Solvent extraction has, of course, been used with flame atomisation in both atomic absorption and atomic fluorescence spectroscopy but the range of suitable solvents (and hence reagents) is somewhat limited by considerations of viscosity, pyrolysis products, and contribution to background radiation. It was considered that these factors should be unimportant when the carbon filament was used for atomisation, for the excess of solvent is removed by rapid preliminary evaporation[1]. Accordingly, a more comprehensive range of solvents and reagents should be possible. The major difficulty envisaged was that the organometallic species might sublime from the filament in molecular form rather than undergo atomisation on the filament.

In this investigation, the atomic fluorescence and atomic absorption of copper, silver, zinc, cadmium and lead has been examined with a number of reagents containing oxygen, nitrogen or sulphur as the donor atoms. Solvents used were methyl isobutyl ketone, chloroform, carbon tetrachloride or benzene.

EXPERIMENTAL

Apparatus

Both atomic absorption and atomic fluorescence measurements were made with a Perkin-Elmer Model 290B spectrophotometer which was coupled either to a Servoscribe recorder or a Tele-equipment Model D53S (storage) oscilloscope. Hollow-cathode lamps (Perkin-Elmer or ASL) were used as spectral sources for all measurements.

The carbon filament unit[2] was mounted on the burner assembly of the spectrophotometer and its position relative to the light path and monochromator slit was adjusted with the burner assembly controls.

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* Part IV: J. Aggett and T. S. West, *Anal. Chim. Acta*, 55 (1971) 359.

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A collimator (2.5 mm diameter, 100 mm long) was placed between the carbon filament and the monochromator slit for atomic absorption measurements. This collimator was fitted with a horizontal entrance slit (0.5 mm wide) which was placed as close as practical to the carbon filament to limit the field of vision.

Extraction procedures

Extraction procedures were carried out as described in the literature[3-5]. In all cases, equal phase volumes were used and the percentage extraction was checked by analysis of the aqueous phase.

Chemicals

Extraction reagents were recrystallised and all water supplies were purified as previously reported[2].

RESULTS AND DISCUSSION

Preliminary results showed that signals obtained with organic extracts were significantly lower than those obtained from aqueous solutions of the same concentration; *e.g.* a 0.1-p.p.m. solution of cadmium dithizonate in chloroform gave a fluorescence intensity about one-third of that obtained for a 0.1-p.p.m. aqueous solution under the same conditions. This was believed to be due to sublimation of undecomposed molecules from the filament.

To overcome this problem, the samples were pretreated on the filament by applying a low voltage (about 2 V) for various lengths of time. For all the extracts examined, the signals then obtained were similar to those of aqueous solutions of the same concentration. Table I shows pretreatment data for the atomic absorption of copper–diethyldithiocarbamate extracts.

TABLE I

EFFECT OF PRETREATMENT OF COPPER–DIETHYLDITHIOCARBAMATE EXTRACT (a.a.s.)[a]

	Pre-treatment	*Signal (mV)*
Organic extract	No heating	12.5
	15 sec/2 V	41.5
	30 sec/2 V	41.5
	60 sec/2 V	42.0
Aqueous solution	No heating	42.0

[a] Atomisation at 8 V and 2 l of argon per min.

The pretreatment necessary to obtain maximal signals varied with the different species, but most were satisfactorily decomposed by application of 2 V for 15–20 sec, and some, such as the pyrrolidinedithiocarbamates, required no preheating at all. Application of 2 V for 15 sec raised the temperature of the filament to 150–180°. No significant increase in temperature was observed when passage of current was continued for longer periods at this voltage.

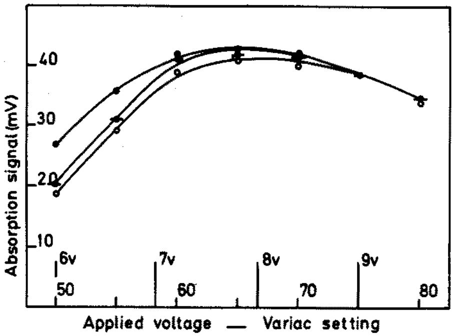
This preliminary heating also served to remove excess of extraction reagent from the filament. This is very necessary for systems such as 10^{-1} *M* oxine in chloroform, where the required element is accompanied by a vast excess of reagent after the solvent has evaporated. The sublimation of the excess (*i.e.* unreacted) reagent is easily followed when the reagent absorbs light of the wavelength used for analysis since this gives rise to a preliminary absorption signal.

With this knowledge the following general procedure was adopted for atomisation of organic extracts.

Samples were placed on the filament with 1- or 5-μl Drummond micro-pipettes and the organic solvent was evaporated, if necessary, by the application of minimal heat. The filament was then immediately heated at 2 V for the pre-determined time and the rod was then allowed to cool for 15 sec before the sample was atomised by application of the appropriate voltage.

The optimal voltages for atomisation were chosen from plots of signal height *vs.* applied voltage, one of which is illustrated in Fig. 1. These data, obtained with a pen-recorder, show that there is no significant difference between the behaviour of organic extracts and aqueous solutions. When the same signals were observed with the oscilloscope, no decrease in signal was observed at higher applied voltage, although the widths of the signal peaks decreased considerably, which suggests that a loss in signal observed with the recorder is due to its slow response.

The variation of atomic absorption signals with height above the filament was examined for aqueous and organic solutions. Figure 2 illustrates the results obtained for various metal complexes in aqueous solutions. It was found that, with the exception of the copper–oxine system (Fig. 3), the differences in the height profiles of aque-



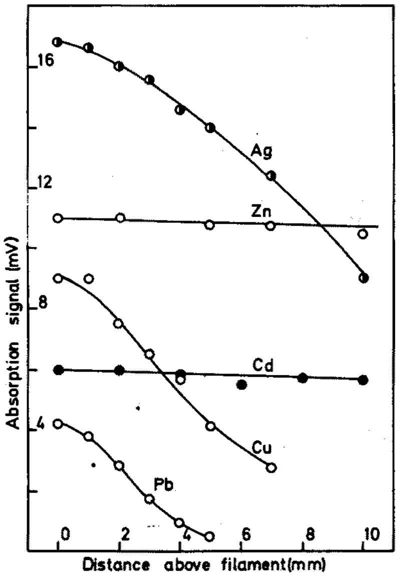
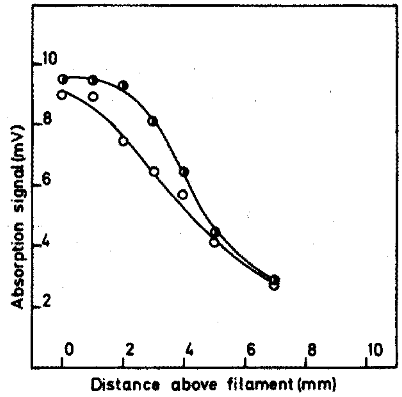


Fig. 1. Absorption signal *vs.* applied voltage. (○) 2 p.p.m. aqueous copper; (●) 2 p.p.m. copper–diethyldithiocarbamate extract in CCl_4; (–●–) 2 p.p.m. copper–pyrrolidinedithiocarbamate extract in MIBK.

Fig. 2. Height profiles of aqueous solutions with argon shielding at 2 l min^{-1}. (Copper) 324.7 nm, applied voltage 8 V; (silver) 328.0 nm, applied voltage 6 V; (zinc) 213.8 nm, applied voltage 6 V; (cadmium) 228.8 nm, applied voltage 6 V; (lead) 283.3 nm, applied voltage 7.2 V.

ous solutions and organic extracts of the same element were marginal. Although the reason for the greater difference observed in the copper–oxine system has not been positively identified, it is conceivable that bis(8-hydroxyquinoline)copper(II) is only partially decomposed by the preliminary heating and that organic species released on subsequent pyrolysis contribute to the absorption signal. Support for this explanation is supplied by TGA and DTA[6,7], which show that in an atmosphere of argon the complex melts without decomposition at 334° and that weight loss occurs slowly at 350–400°.



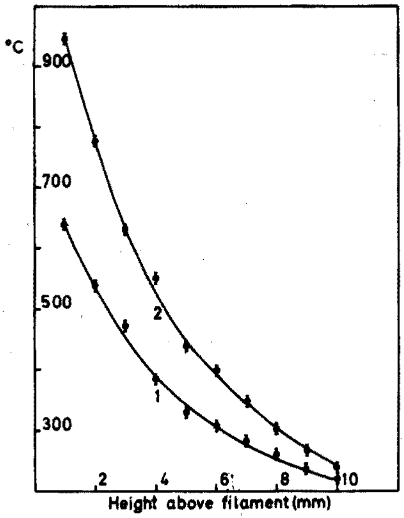


Fig. 3. Height profiles with argon shielding at 2 l min^{-1}. (○) 2 p.p.m. aqueous copper solution (324.7 nm, 8 V); (◑) 2 p.p.m. copper oxine extract in chloroform (324.7 nm, 8 V).

Fig. 4. Temperature profiles. (1) Argon 2 l min^{-1}, 6 V for 4 sec; (2) argon 2 l min^{-1}, 8 V for 3 sec.

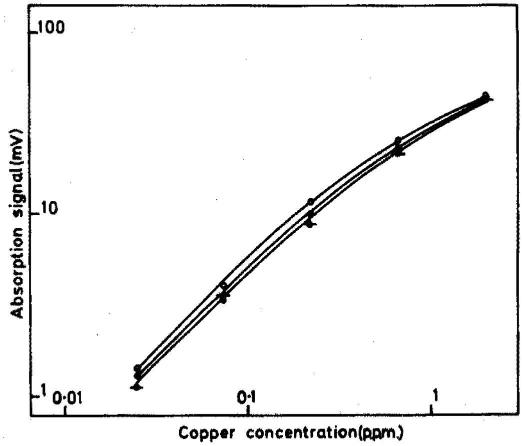


Fig. 5. Calibration curves for copper (324.7 nm, 8 V). (○) Dithizone extracts in carbon tetrachloride; (●) pyrrolidinedithiocarbamate extracts in methyl isobutyl ketone, (–●–) diethyldithiocarbamate extracts in carbon tetrachloride.

The height profiles also indicate that in these systems free atoms exist in significant quantities for several millimetres above the filament despite the relatively low temperatures in this region (Fig. 4). Data from the height profiles were used to select optimal conditions for subsequent work. For the silver, zinc and cadmium systems, measurements were made 2 mm above the filament; measurements on the copper and lead systems were made 1 mm above the filament.

TABLE II

ATOMIC ABSORPTION AND ATOMIC FLUORESCENCE OF ELEMENTS IN ORGANIC EXTRACTS

Element	*System*	*Conditions*	*Detection limits*[a]	
			A.a.s. (p.p.m.)	*A.f.s. (p.p.m.)*
Copper	Aqueous	324.7 nm	0.01	0.004
	Thenoyltrifluoroacetone/C_6H_6	8 V[b]	0.01	0.004
	8-Hydroxyquinoline/$CHCl_3$	Argon 2 l min^{-1}	0.01	0.004
	Dithizone/CCl_4	A.S.L. High-	0.01	0.004
	Diethyldithiocarbamate/CCl_4	intensity	0.01	0.004
	Pyrrolidinedithiocarbamate/MIBK	H.C.L.	0.01	0.004
	Cupferron/$CHCl_3$		0.01	0.004
Silver	Aqueous	328.0 nm	0.003	0.001[c]
	Dithizone/CCl_4	6 V	0.003	0.001
	Diethyldithiocarbamate/CCl_4	Argon 2 l min^{-1}	0.003	0.001
		H.C.L.		
Zinc	Aqueous	213.8 nm	0.002	0.001[c]
	Thenoyltrifluoroacetone/C_6H_6	6 V	0.002	0.001
	8-Hydroxyquinoline/$CHCl_3$	Argon 2 l min^{-1}	0.002	0.001
	Dithizone/CCl_4	H.C.L.	0.002	0.001
	Diethyldithiocarbamate/CCl_4		0.002	0.001
	Pyrrolidinedithiocarbamate/MIBK		0.002	0.001
Cadmium	Aqueous	228.8 nm	0.005	0.001[c]
	8-Hydroxyquinoline/$CHCl_3$	6 V	0.005	0.001
	Dithizone/CCl_4	Argon 2 l min^{-1}	0.005	0.001
	Diethyldithiocarbamate/CCl_4	H.C.L.	0.005	0.001
Lead	Aqueous	283.3 nm	0.08	0.01[c]
	Dithizone/CCl_4	7.2 V	0.08	0.01
	Pyrrolidinedithiocarbamate/MIBK	Argon 2 l min^{-1}	0.08	0.01
		H.C.L.		

[a] Taken as signal : noise = 2 :1. [b] Atomization voltage. [c] These detection limits in fluorescence were obtained with normal hollow-cathode lamps and therefore do not represent the maximum sensitivity available by a.f.s.

Table II contains a list of the organic extracts studied, together with their detection limits in both atomic absorption and atomic fluorescence. The relatively poor detection limits for Ag, Cd, Pb, Zn in atomic fluorescence stem from the use of conventional hollow-cathode lamps at low current (10 mA) for examination of these systems.

Atomic absorption calibration curves for some of the copper extracts are shown in Fig. 5. Although these were obtained at different times they were each compared directly with those of aqueous samples and no significant differences were observed.

While the precision obtained with more concentrated solutions was generally reasonable (±3–5%) in both atomic absorption and atomic fluorescence, it was, of course, less satisfactory in the vicinity of the detection limit, owing to the slow response rate of the recorder (*ca.* 0.8 sec f.s.d.) in comparison to the lifetime of the atomic signal ($t_{\frac{1}{2}}$ *ca.* 0.02–0.05 sec).

The results obtained in this work demonstrate that the carbon filament is most useful for the analysis of a variety of organic extracts.

Several of the solvents used in this study are not convenient for aspiration into flames, *e.g.* $CHCl_3$, CCl_4, C_6H_6, thus demonstrating the flexibility of the filament atom reservoir technique. Additionally, the variety of ligands used, illustrates that the technique should be successful for most extracting agents.

Dilute solutions can of course be concentrated on the carbon filament by repeated additions of aliquots of 1–5 μl of aqueous solutions, evaporating the water between additions by passage of current at a low voltage, but the present study also shows that the technique can be used with the normal solvent extraction process of preconcentration of trace elements. This would be particularly beneficial for separation of traces from matrices of high solid content.

One of us (J.A.) is grateful to the Nuffield Foundation who have supported this work by the award of a Travelling Fellowship in Science.

SUMMARY

The behaviour of the carbon filament atom reservoir in the atomic absorption and atomic fluorescence of trace metals (Ag, Cd, Cu, Pb, Zn) extracted from aqueous solutions into organic solvents (C_6H_6, $CHCl_3$, CCl_4, MIBK) by a variety of chelating agents (cupferron, dithiocarbamates, dithizone, 8-hydroxyquinoline, thenoyltrifluoroacetone) is described. There is no restriction on the nature of the solvent as in flame-based techniques and the behaviour of the organometallic systems is virtually identical to that of aqueous solutions of the metals. Only with the copper(II)–oxine system was a slightly anomalous behaviour observed. The general technique may easily be applied with solvent extraction preconcentration systems.

RÉSUMÉ

On examine le comportement du réservoir atomique à filament de carbone dans l'absorption atomique et la fluorescence atomique de traces de métaux (Ag, Cd, Cu, Pb, Zn), extraits de solutions aqueuses dans des solvants organiques (C_6H_6, $CHCl_3$, CCl_4, methylisobutylcétone) en présence de divers réactifs chélatants (cupferron, dithiocarbamates, dithizone, hydroxy-8-quinoléine, thénoyltrifluoracétone). Il n'y a pas de restriction sur la nature du solvant comme dans le cas des techniques à flamme; le comportement des systèmes organométalliques est pratiquement identique à celui de solutions aqueuses. Cependant on observe une légère anomalie pour le système cuivre(II)–oxine. Cette technique permet donc une préconcentration préalable par extraction dans un solvant.

ZUSAMMENFASSUNG

Es wird das Verhalten einer Kohlefaden-Atomisierungsvorrichtung bei der Atomabsorption und Atomfluoreszenz von Spurenmetallen (Ag, Cd, Cu, Pb, Zn) beschrieben, die aus wässrigen Lösungen unter Verwendung verschiedener Chelatisierungsmittel (Kupferron, Dithiocarbamate, Dithizon, 8-Hydroxychinolin, Thenoyltrifluoraceton) mit organischen Lösungsmitteln (C_6H_6, $CHCl_3$, CCl_4, MIBK) extrahiert worden sind. Eine Einschränkung bezüglich der Art des Lösungsmittels wie bei Flammenverfahren ist nicht vorhanden; die organometallischen Systeme verhalten sich praktisch wie die wässrigen Lösungen der Metalle. Ein etwas ungewöhnliches Verhalten wurde nur beim Kupfer(II)–Oxin-System beobachtet. Das allgemeine Verfahren kann leicht auf der Anreicherung dienende Lösungsmittelextraktionssysteme angewendet werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF NANOGRAM QUANTITIES OF MERCURY BY THE REDUCTION-AERATION METHOD AND ATOMIC FLUORESCENCE SPECTROPHOTOMETRY

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(Received 7th June 1971)

Flameless methods for the determination of mercury by atomic absorption were recently reviewed by Manning[1]. Of the various techniques the most widely reported is the tin(II) reduction–aeration method. Several papers describing the use of this method have appeared since Manning's review[2–4]. The present paper describes an atomic fluorescence measurement finish to the reduction–aeration method.

EXPERIMENTAL

Apparatus

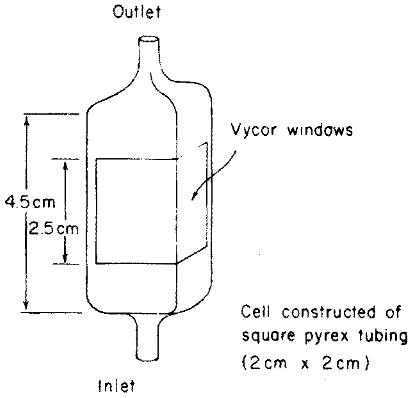
The instrumentation used is listed below.

Excitation source	Fluorescence—Hg pen-lamp, Ultra Violet Products, Inc.; Absorption—hollow-cathode discharge tube, Perkin–Elmer Corp.
External optics	Fluorescence—30-mm diameter, 50-mm focal length, fused silica lens; Absorption 30-mm diameter, 100-mm focal length, fused silica lenses.
Spectrometer	Heath EU-700 scanning monochromator, 350 mm Czerny-Turner mounting, 1180 grooves mm^{-1} grating blazed for 2500 Å, f/7, 20 Å mm^{-1} reciprocal linear dispersion at exit slit in 1st order, ganged entrance and exit bilaterally adjustable straight slits.
Detector	R166 solar blind multiplier phototube, Hamamatsu TV, 1600–3200 Å spectral response.
Detector power supply	Heath EU-701, 300–1500 V d.c., 0–1.5 mA.
Amplifier	Solid state nanoammeter, 10^{-5}–10^{-11} A full scale, locally constructed after circuit described by O'Haver and Winefordner[5].
Recorder	Texas Instrument Co., 1 mA galvanometric.
Pump	Manostat Corp., Varistaltic 72-895-00.
Fluorescence cell	Square pyrex 2-cm tubing with 2 × 2.5 cm Vycor windows on two adjacent sides (see Fig. 1).
Absorption cell	Pyrex round tubing, 20 cm long, 2.5 cm o.d., with Suprasil windows.

The form of the atomic fluorescence vapor cell is shown in Fig. 1. For atomic fluorescence measurements the cell was placed as close as possible to the entrance slit of the monochromator with the cell center aligned with the slit. The mercury lamp was placed at 90° to the line of observation of the monochromator, and a 50-mm focal length lens was used to form a 1:1 image of the source *ca.* 2 cm beyond the cell. A blackened cylindrical shield was used between lamp and lens to reduce the amount of randomly reflected radiation reaching the detector.

For atomic absorption measurements a 20-cm long, 2.5-cm o.d. absorption cell with fused silica windows was used. Lenses of 100 mm focal length were used on both sides of the absorption tube to form a 1:1 image of the mercury hollow-cathode discharge in the center of the absorption tube and on the entrance slit of the monochromator.

The arrangement of components in the gas train is indicated schematically in Fig. 2. The reduction–aeration system is similar to that described elsewhere (*e.g.* by Hatch and Ott[6]).



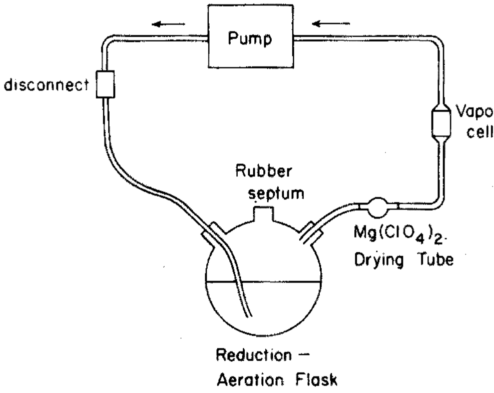


Fig. 1. Vapor cell for fluorescence measurements.

Fig. 2. Gas train for reduction–aeration method.

Standard mercury solutions

All standards were prepared from mercury(II) chloride. A stock solution of 100 μg ml^{-1} was prepared by dissolving 0.1354 g of mercury(II) chloride and diluting to 1 l with 0.5 *M* sulfuric acid. Two drops of 5% (w/v) potassium permanganate solution were added to each mercury solution. All solutions were stored in polyethylene containers.

Procedure

For the reduction–aeration procedure mercury must be present in solution as mercury(II). Samples requiring digestion were treated by the permanganate–peroxydisulfate oxidation method described elsewhere[7]. Sample digestions were carried out overnight. When measurements were to be made, excess of oxidant in standards and digested samples was removed by addition of 25% (w/v) hydroxyammonium chloride solution, and 50 ml of solution was placed in the reduction–

aeration flask. The system was closed after addition of the solution, 3 ml of a 10% (w/v) solution of tin(II) chloride in 0.25 *M* sulfuric acid was added to the solution by syringe through the rubber septum, and the pump was started immediately. A steady signal was obtained within 1 min. Flow rates of 2.6–5 l $\min^{-1}$ of air were investigated, and the flow rate was found not to be a critical factor in either the reproducibility or sensitivity of the measurements. A flow rate of 4.0 l $\min^{-1}$ was used for the measurements reported. Approximately 2 min after pumping was started, the system was opened, and the mercury vapor flushed out of the vapor cell.

RESULTS AND DISCUSSION

Effect of slit width

The effect of slit width on the signal intensity was investigated to determine the optimal setting. Figure 3 shows the effect of slit width on the measured fluorescence signal and signal-to-background ratio for a 70-ng sample. The signal increases linearly with slit width over the range 100–2000 μm slit width. The background signal is due chiefly to randomly reflected 253.7-nm radiation reaching the detector. There was no measurable noise associated with the background signal at slit widths of 1000 μm or less. All subsequent fluorescence measurements were made with a slit width of 500 μm.

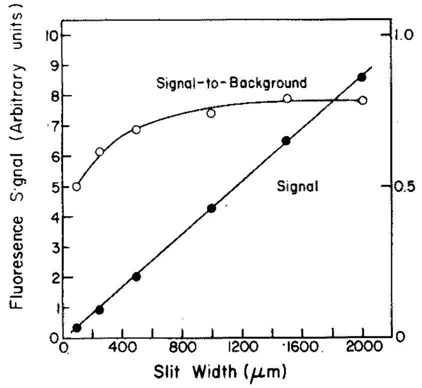


Fig. 3. Effect of slit width on fluorescence signal and signal-to-background ratio for a sample containing 70 ng Hg.

The ultimate extension of the slit-width study is a non-dispersive system in which an aperture of several millimeters diameter would replace the slit, and the spectral bandpass would be determined, in our system, by the spectral response of the R166 solar blind multiplier phototube. The advantages of a non-dispersive system have been discussed previously[8].

Analytical curves

Figure 4 shows a typical recorder tracing of the atomic fluorescence signals. The fluorescence signal was taken as the difference between the plateau height and the baseline. Analytical curves, as shown in Fig. 5, were prepared from the averaged

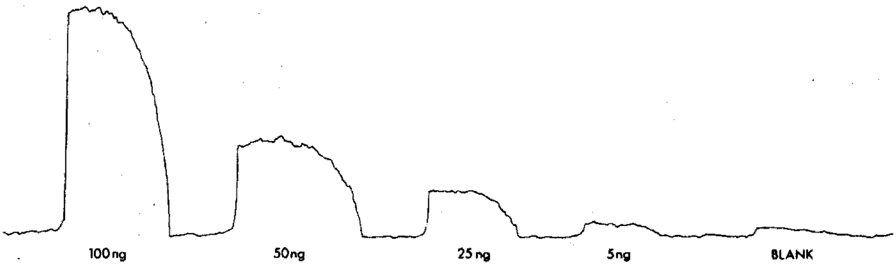


Fig. 4. Typical recording tracing for fluorescence signals.

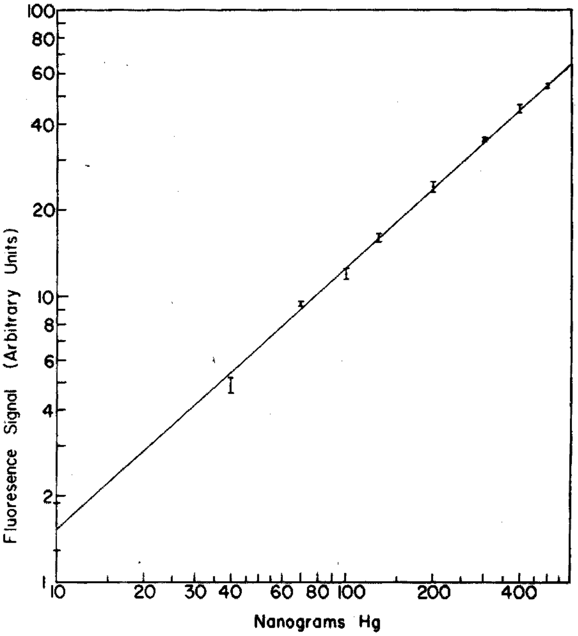


Fig. 5. Analytical curve for fluorescence.

values of 3 replicates for each quantity of mercury. Blank readings were subtracted from each of the other readings before plotting. In all cases the amount of mercury shown was present in 50 ml of solution.

The limit of detection was estimated to be 3 ng (0.06 p.p.b.), and mercury could be determined at the 15-ng level. Analytical curves were linear from the limit of detection to the highest amount measured, 600 ng.

Precision

In order to test the long-term reproducibility of the technique, the fluorescence signal for each of four samples was read twice a day for six consecutive days. The system was not restandardized during this six-day period. The calculated relative standard deviations were found to be 7% for 40 ng Hg, 3% for 70 and 100 ng Hg and 2% for 130 ng Hg.

Determinations in typical samples

The reduction–aeration atomic fluorescence technique was used for the determination of mercury in natural waters, sediments, and standard rock samples. Some typical results are shown in Tables I–III.

Table I shows the results of a recovery study utilizing a water sample taken from the channel bottom of Mobile Bay. The blank samples were 0.5 *M* sulfuric acid prepared from distilled water and reagent-grade sulfuric acid. An analytical curve was prepared from the "Blank" set after first subtracting the 0-ng reading from each of the other readings in the set. The Mobile Bay samples were acidified on collection. The mercury contents for the bay samples were read from the analytical curve after similarly subtracting the 0-ng "Blank" reading from the readings shown in Table I.

TABLE I

RECOVERY OF MERCURY IN MOBILE BAY WATER SAMPLE

Sample	*Hg added (ng)*	*Fluorescence signal*	*Hg found (ng)*
Blank	0	0.15	
Blank	50	1.93	
Blank	100	3.70	
Blank	150	5.48	
Blank	200	7.38	
Bay water	0	0.35	5
Bay water	100	3.87	104

TABLE II

DETERMINATION OF MERCURY IN SEDIMENT SAMPLES BY ATOMIC FLUORESCENCE AND ATOMIC ABSORPTION

Sample number	*Atomic fluorescence*		*Atomic absorption*	
	Sample weight (g)	*Hg found (p.p.m.)*	*Sample weight (g)*	*Hg found (p.p.m.)*
1	0.301	0.22	0.823	0.24
	0.280	0.27	0.971	0.27
2	0.238	0.27	1.614	0.29
	0.289	0.30	1.131	0.27
3	0.318	0.24	1.083	0.19
	0.227	0.20	1.009	0.23

Table II shows a selection of results for mercury determinations in sediment samples taken from the bottom of St. Joseph's Bay, Florida. Determinations were carried out on four portions of each sample, two by fluorescence and two by absorption. Absorption results were obtained with a Perkin–Elmer Model 303 atomic absorption spectrophotometer suitably modified for the reduction–aeration technique[6]. There is satisfactory agreement between the duplicate determinations and between the two methods. Note that the greater sensitivity of the fluorescence technique made possible a substantial reduction in the sample size required.

Table III compares the results obtained in this study with other reported re-

TABLE III

COMPARISON OF RESULTS OF THIS STUDY WITH OTHER RESULTS FOR A STANDARD ROCK SAMPLE[a]

Hg found (p.p.m.)			
This study	*Atomic absorption*[6]	*Neutron activation*[9]	*Dithizone spectrophot.*[6]
0.18	0.18; 0.18	0.17	0.17; 0.16

[a] United States Geological Survey W-1.

sults for a standard rock sample. The rock standard was the W-1 rock issued by the United States Geological Survey. The result reported for this study is the average of six determinations. The standard deviation of the mean is 0.01 p.p.m.

Comparison of atomic absorption and atomic fluorescence measurements

For comparison purposes absorption measurements were made with the measurement system designed for fluorescence, but the square cell and pen-lamp source were replaced by a 20-cm long absorption cell and a mercury hollow-cathode source appropriately arranged for absorption measurements. A recorder tracing of absorption signals with 2 × scale expansion is shown in Fig. 6, and the absorption analytical curve is shown in Fig. 7, curve A. A scale expansion of approximately 10 ×

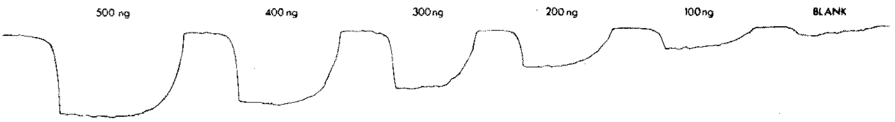


Fig. 6. Typical recorder tracing for absorption measurements.

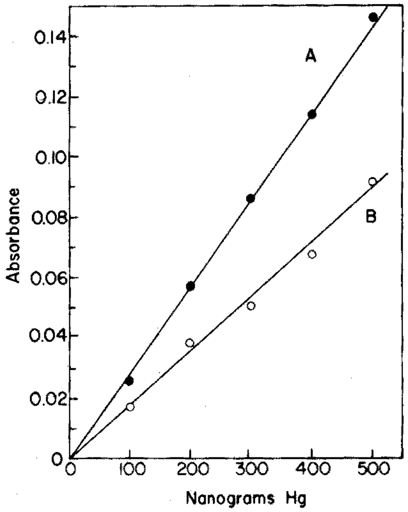


Fig. 7. Analytical curves for absorption. (A) Hollow-cathode discharge tube spectral source; (B) pen-lamp spectral source.

is required to achieve sensitivity equalling that of the fluorescence method, and, as shown in Fig. 6, the blank reading problem is more serious in absorption than it is in fluorescence. The larger blank effect is presumably due to the greater effect of broad band absorption and scatter in the long path cell.

Atomic absorption and fluorescence differ in their requirements for an excitation source. For absorption a narrow line source is required to achieve high sensitivity; for fluorescence the line width is unimportant but the source intensity must be high over the frequency range of maximum absorption. This difference is well-illustrated in the determination of mercury. The cheap mercury pen-lamp is intense, and quite stable in output. It is well-suited to fluorescence measurements but less well-suited for absorption measurements. Curve B of Fig. 7 shows the analytical curve obtained when the pen-lamp was used for absorption measurements. The decrease in sensitivity is presumably due to the greater width of the Hg 253.7-nm line produced by the pen-lamp. The pen-lamp was approximately 10^3 times more intense than the hollow-cathode discharge tube.

We wish to express our thanks to Anders Andren of the Department of Oceanography, Florida State University, for providing us with the Mobile Bay and St. Joseph's Bay samples, and for measurements on the sediment samples. This work was supported in part by funds from PHS Grant RO1 GM15996-03 from the National Institute of General Medical Sciences.

SUMMARY

An atomic fluorescence measurement in conjuction with the reduction–aeration method for the determination of mercury is described. The detection limit is 3 ng Hg (0.06 p.p.b.). The technique is useful for analysis of samples containing 15–600 ng Hg. The results of determinations in water, sediment, and rock samples are described, and the atomic fluorescence and atomic absorption techniques are compared.

RÉSUMÉ

On décrit une méthode de dosage du mercure, en quantité de l'ordre du nanogramme, par spectrophotométrie de fluorescence atomique. La limite de détection est de 3 ng Hg (0.06 p.p.b.). Cette technique est intéressante pour l'analyse d'échantillons contenant 15 à 600 ng Hg. Les résultats obtenus pour l'analyse de l'eau, de sédiments et de roches sont donnés. Une comparaison est faite avec la spectrophotométrie par absorption atomique.

ZUSAMMENFASSUNG

Es wird eine Atomfluoreszenzmessung in Verbindung mit der Methode der Reduktion und Luftdurchleitung für die Bestimmung von Quecksilber beschrieben. Die Nachweisgrenze ist 3 ng Hg (0.06 p.p.b.). Das Verfahren eignet sich für die Analyse von Proben mit 15–600 ng Hg. Die Ergebnisse von Bestimmungen in Wasser-, Sediment- und Gesteinsproben werden vorgelegt und die Verfahren der Atomfluoreszenz und Atomabsorption miteinander verglichen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

INTERFERENCES IN THE DETERMINATION OF TITANIUM, ZIRCONIUM, AND HAFNIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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(Received 12th October 1970)

In the determination of elements by atomic absorption spectrometry (a.a.s.), spectral interferences are generally expected to be absent. However, the presence of species which alter the concentration of the ground-state metal atoms of the analyte in the flame, will give rise to differences in the atomic absorption signal. Such changes in the absorption are generally termed chemical interferences.

A few studies of this type of interference in the atomic absorption determination of titanium, zirconium, and hafnium have appeared in the published literature, after it had been shown that such refractory metals could be atomized in the reducing oxygen–acetylene[1,2] and nitrous oxide–acetylene[3,4] flames. Amos and Willis[4] observed that the fluoride ion and iron enhanced the absorption by titanium, zirconium, and hafnium in both nitrogen–oxygen–acetylene and nitrous oxide–acetylene flames. Bowman and Willis[5] found that iron in the presence of concentrations of sulphuric acid below 0.5 *M* depressed the absorption of titanium, but caused an enhancement at higher acid concentrations. The maximum enhancement was observed with 2 *M* acid, the effect being very much dependent on flame stoichiometry. These investigators also observed that aluminium and sulphuric acid enhanced titanium absorption. The enhancement of titanium absorption by iron and aluminium was also observed[6,7] in the determination of titanium in various iron alloys. Nitrogen-containing compounds[8] and lanthanum[9] have been found to enhance zirconium absorption. Sastri *et al.*[10] have discussed many of these chemical interferences in terms of polynuclear oxygen-bonded species.

However no detailed study of the interferences of all the three elements titanium, zirconium, and hafnium has appeared in the literature, and the present work is intended primarily as an investigation of the various interferences on the absorption of these metals in nitrous oxide–acetylene flames. The effects of various cationic and anionic species which are usually associated with these analytes under practical conditions are studied and an attempt is made to correlate the interesting behaviour of these chemically similar elements.

EXPERIMENTAL

Instrumentation

The atomic absorption measurements were carried out with a Techtron AA-4

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atomic absorption spectrometer. The standard Techtron nebulizer and spray chamber system was employed, along with the AB-52 grooved head burner for supporting the nitrous oxide–acetylene flame. Hollow-cathode lamps were supplied by Atomic Spectral Lamps Pty. Ltd. Gas flow rates were adjusted for maximum absorption signal for each element. Height in the flame was measured relative to the point where the burner head just started to cut off the light beam from the hollow-cathode lamp. The various experimental parameters are summarized in Table I. In all cases a fairly fuel-rich flame was used, the interconal zone being about 20 mm high.

TABLE I

EXPERIMENTAL PARAMETERS

Element	*Wavelength (nm)*	*Lamp current (mA)*	*SBW (nm)*	*Ht. of observation in flame (mm)*
Ti	364.27	15	0.08	1.0
Zr	360.12	10	0.08	2.0
Hf	307.29	5	0.08	2.0

Reagents

Solutions of titanium, zirconium, and hafnium were prepared by dissolving the metal (99.9% purity or better) in a few drops of hydrofluoric acid and 2 ml of nitric acid and, unless otherwise stated, the final solutions contained about 0.1% of each acid. In addition to increasing the analytical sensitivity this also helped to approximate the conditions which usually exist when these elements are determined in routine samples.

Solutions of other substances were prepared from "Specpure" or "AnalaR" grade materials and acids. The metal or a suitable salt was usually dissolved in 5% hydrochloric acid followed by addition of a few drops of nitric acid to obtain a 10,000 μg ml^{-1} stock solution of the metal.

RESULTS

Titanium

The absorbance of a titanium solution (100 μg ml^{-1}) was not affected by hydrochloric acid below a concentration of 2 *M*, but decreased slightly at higher concentrations. Nitric acid (0.5 *M*) reduced the absorbance by 8%, but higher acid concentrations had no further effect. Sulphuric acid at concentrations up to about 2 *M* enhanced the titanium absorption but higher concentrations showed a depressing effect, the absorbance in 9 *M* acid being only half the original value. Acetic acid, surprisingly, produced a considerable enhancement of the titanium absorption. Hydrogen peroxide did not affect the titanium absorption but phosphoric and hydrofluoric acids caused an enhancement, the effect, however, reaching a saturation level. Low concentrations of ammonia (up to 0.05%) caused an enhancement, but at higher concentrations the absorbance fell, probably owing to the precipitation of titanium as the hydroxide.

The effects of various metallic ions on the absorption of titanium (100 μg ml^{-1}) were investigated by adding varying amounts of the respective ions and comparing the absorbance obtained with the absorbance of titanium alone. As observed by others[7], it was found that most of the ions added enhanced titanium absorption. Further, the results indicated a regular effect from the various members of a periodic sub-group. These observations are detailed below.

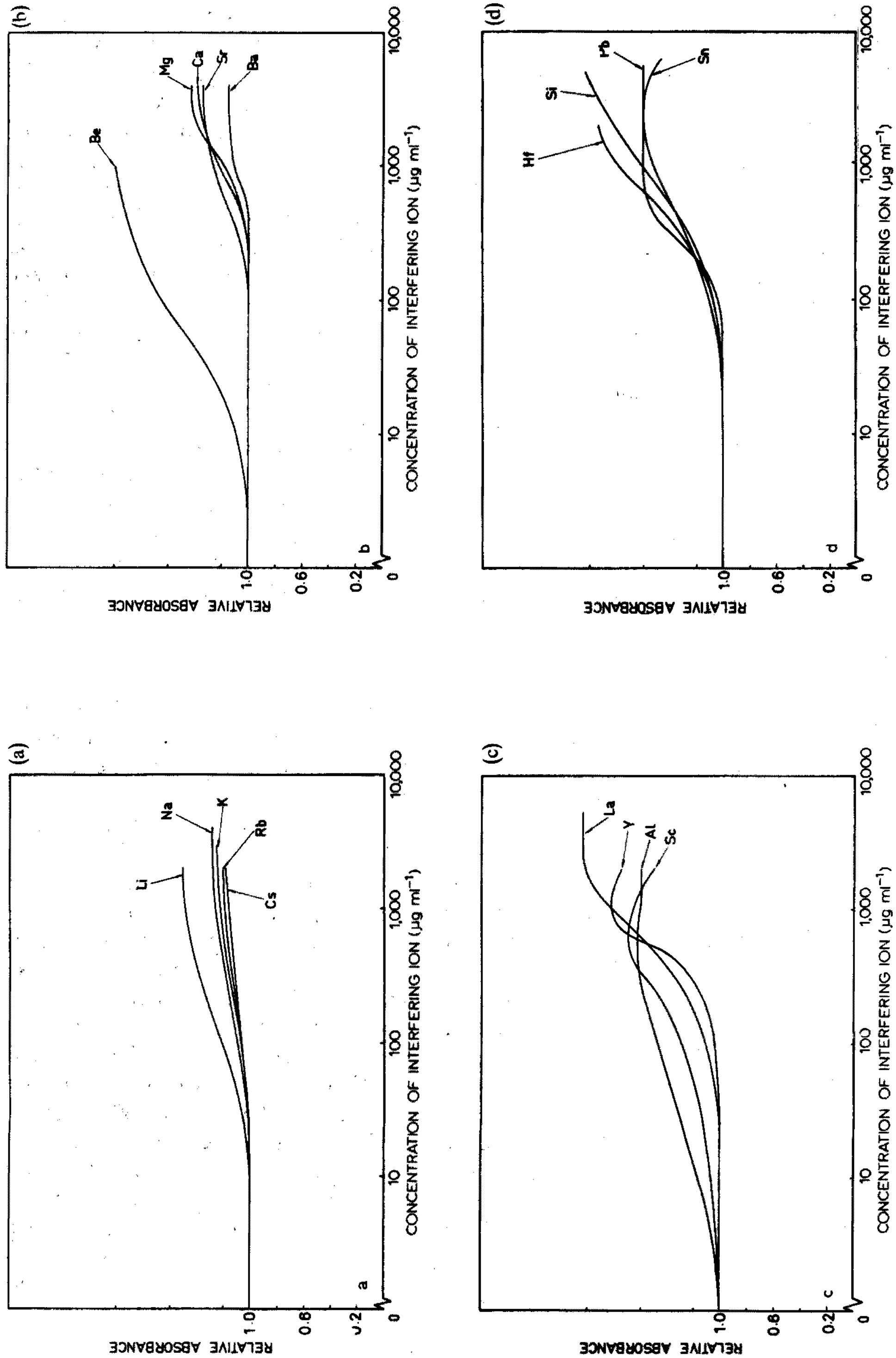
The effects of various alkali and alkaline earth metals on the absorbance of titanium are shown in Fig. 1(a, b). Maximum enhancement was produced by the smallest ion, beryllium (*cf.* lithium), whereas barium produced the least enhancement. Changes in titanium absorbance produced by Group III elements are shown in Fig. 1(c). The effect of aluminium is apparent even at concentrations as low as 10–100 μg ml^{-1}. Boron, however, depressed titanium absorption considerably even at very low concentrations. The addition of Group IV elements again enhanced titanium absorption (Fig. 1(d)). The enhancements produced by silicon and hafnium were very much greater than expected, partly because of the effect of 2% hydrofluoric acid present in the solutions of the added metals. In any case the acid alone would not be expected to enhance the absorption to such an extent. Figures 1(e) and (f) show the effects produced by various transition elements. The enhancement by vanadium, manganese, and zinc reached a saturation level at about 1000 μg ml^{-1} of the added metal. Iron, chromium, and copper showed maximum effect at about 1000 μg ml^{-1}, above which the absorbance dropped. The effect of adding tungsten is unusual in that small concentrations decreased the absorption of titanium but higher amounts caused enhancement. This probably occurs because of an increase in the fluoride concentration (*cf.* silicon, hafnium).

Zirconium

The effects of nitric acid, hydrochloric acid, and hydrofluoric acid on zirconium were similar to those reported for titanium. Sulphuric acid, however, seemed to reduce the absorption of zirconium. Acetic acid and ammonia enhanced the absorption, whereas hydrogen peroxide had no appreciable effect.

The effects of different metallic ions on the absorption of zirconium (500 μg ml^{-1}) were as follows.

Alkali metal elements depressed the absorption of zirconium solutions in the order Li > Na > K > Rb > Cs, the last having a very slight effect even at a concentration of about 1000 μg ml^{-1}. Similar effects were observed from members of the alkaline earth series; the order of the depressing effect was Be > Mg > Ca > Sr > Ba. These effects are illustrated in Fig. 2(a, b). Addition of Group III elements generally depressed the absorption of zirconium, the effect decreasing with increase in the atomic number of the additive. Lanthanum at a concentration about equal to that of zirconium actually enhanced the absorption. These effects are shown in Fig. 2(c). The effects of adding Group IV elements are shown in Fig. 2(d). Tin at about 500 μg ml^{-1} depressed the absorption. Titanium and lead had no appreciable effect, whereas an enhancement was caused by silicon and hafnium. The depressing effects of adding uranium and thorium are illustrated in Fig. 2(e). Vanadium caused a depression, niobium had no appreciable effect, and tantalum caused an enhancement (Fig. 2(f)). In Figs. 2(g) and (h) are shown the effects of various transition elements on the absorption of zirconium which once again are in the order of atomic numbers, *e.g.* chromium produced a much greater depression than tungsten. Iron decreased the absorption very considerably whereas copper increased it.


(a)
a
Li
Na
K
Rb
Cs
(b)
b
Be
Mg
Ca
Sr
Ba
(c)
c
La
Y
Al
Sc
(d)
d
Hf
Si
Pb
Sn
RELATIVE ABSORBANCE
1.0
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CONCENTRATION OF INTERFERING ION (μg ml^{-1})

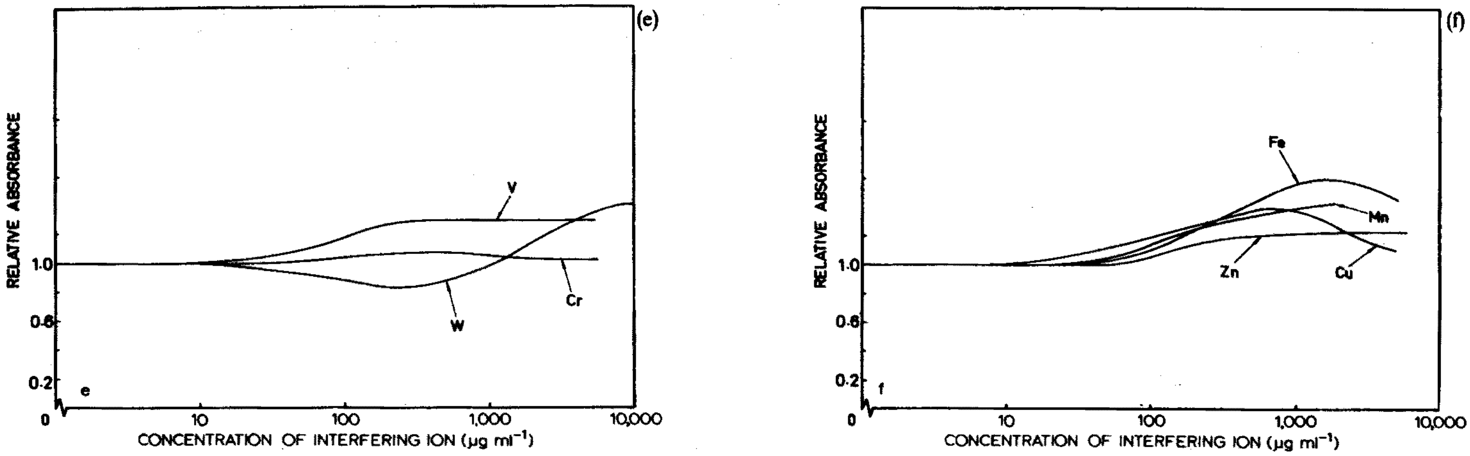
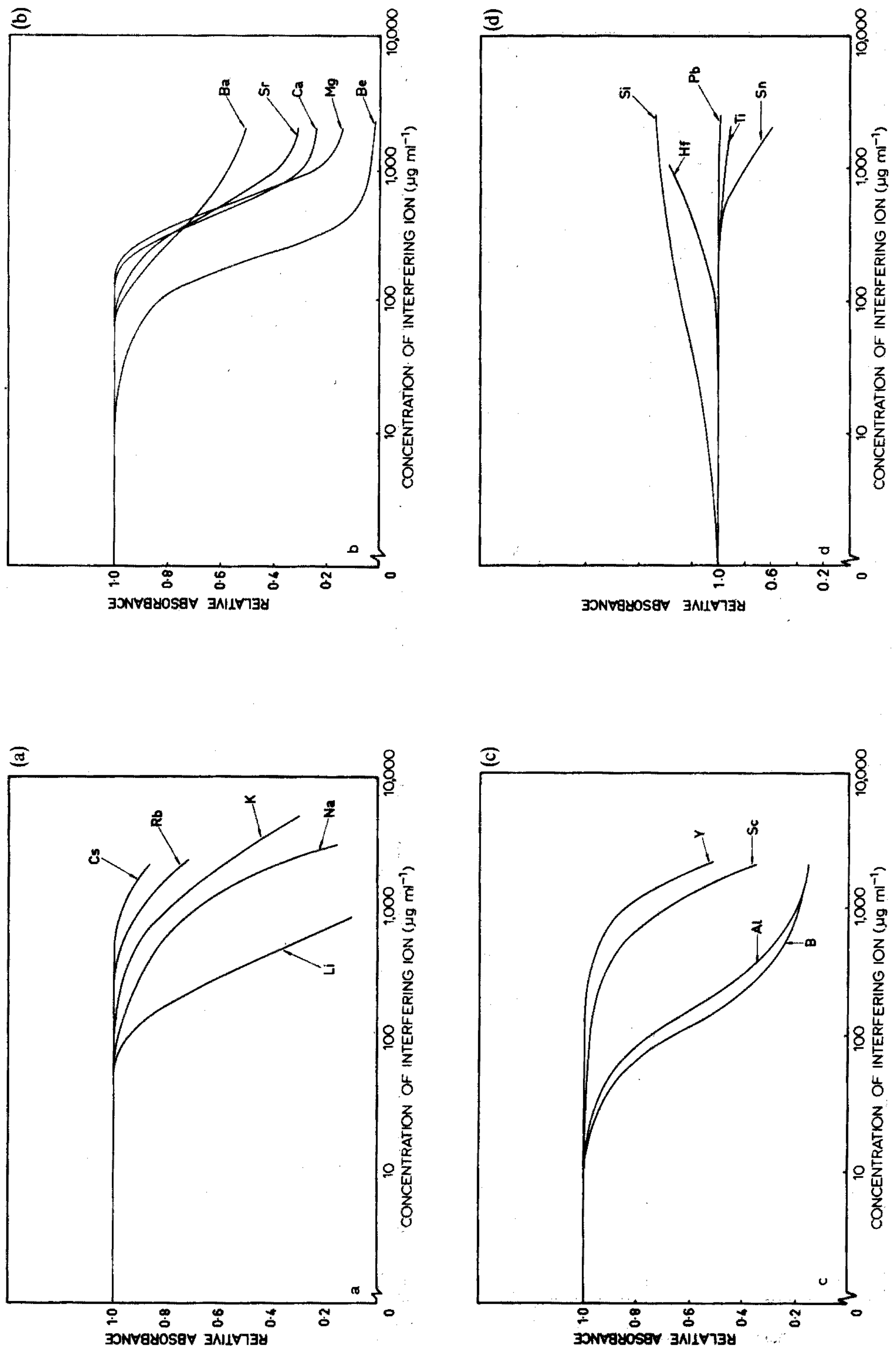


Fig. 1. Effect of various elements on the absorbance of titanium. (a) Alkali metals; (b) alkaline earth metals; (c) Group III elements; (d) Group IV elements; (e) vanadium, chromium and tungsten; (f) various transition elements.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100
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CONCENTRATION OF INTERFERING ION (μg ml^{-1})
(b)
b
Ba
Sr
Ca
Mg
Be
RELATIVE ABSORBANCE
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0·8
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CONCENTRATION OF INTERFERING ION (μg ml^{-1})
(c)
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RELATIVE ABSORBANCE
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CONCENTRATION OF INTERFERING ION (μg ml^{-1})
(d)
d
Si
Pb
Hf
Ti
Sn
RELATIVE ABSORBANCE
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CONCENTRATION OF INTERFERING ION (μg ml^{-1})

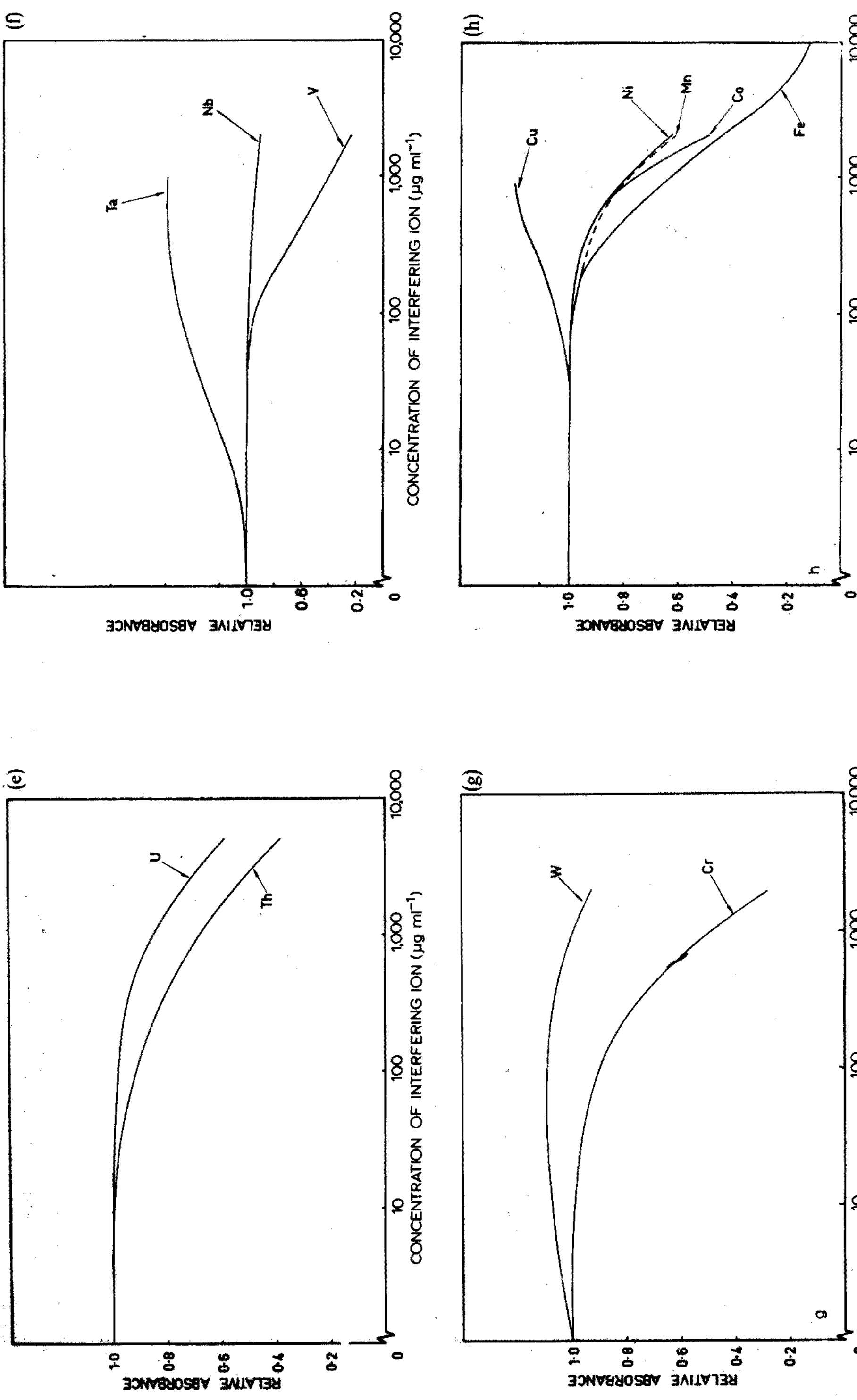
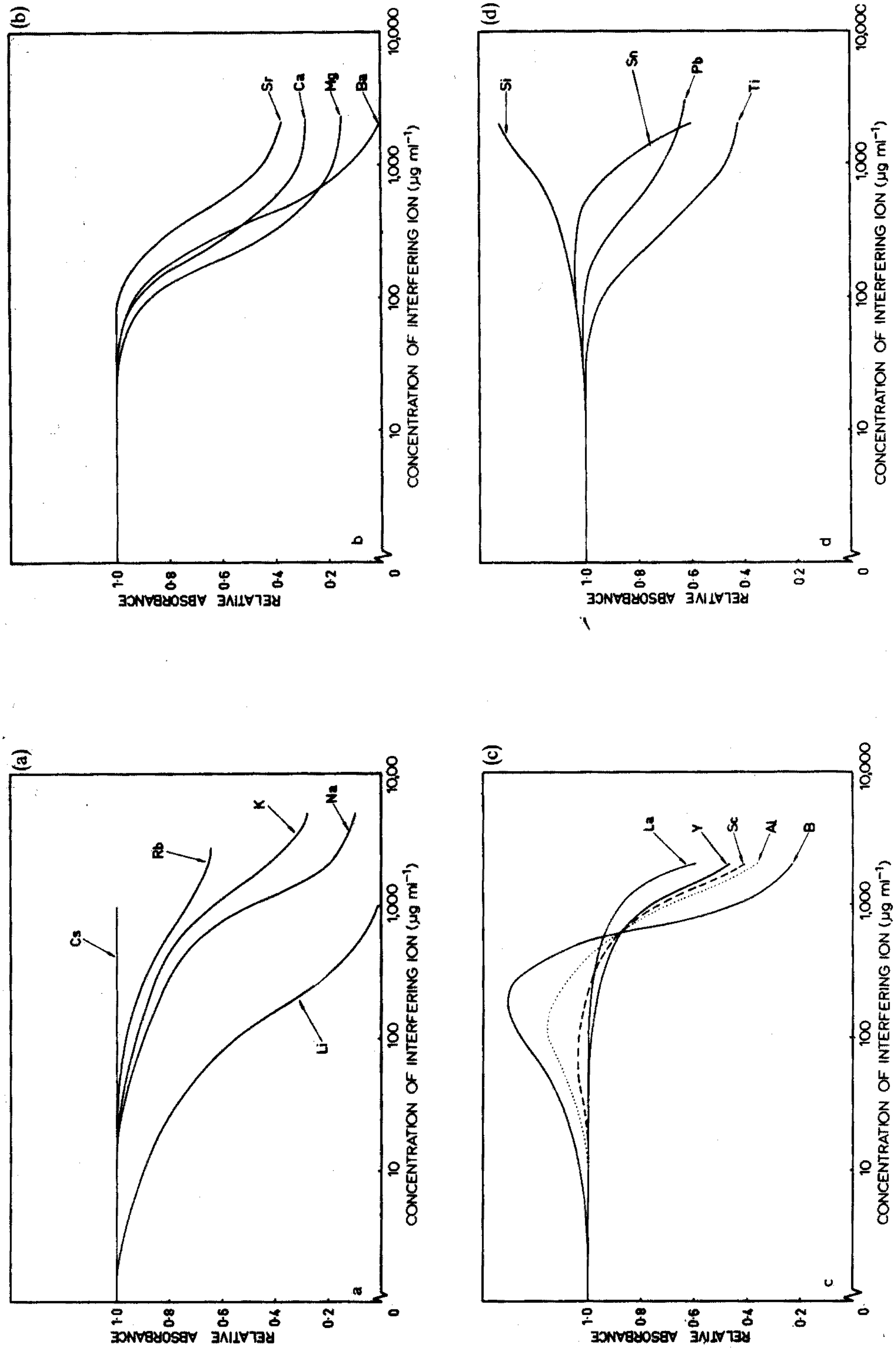


Fig. 2. Effect of various elements on the absorbance of zirconium. (a) Alkali metals; (b) alkaline earth metals; (c) Group III elements; (d) Group IV elements; (e) uranium and thorium; (f) Group V elements; (g) Group VI elements; (h) various transition elements.


(a)
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RELATIVE ABSORBANCE
1·0
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CONCENTRATION OF INTERFERING ION (μg ml⁻¹)
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B
Si
Sn
Pb
Ti

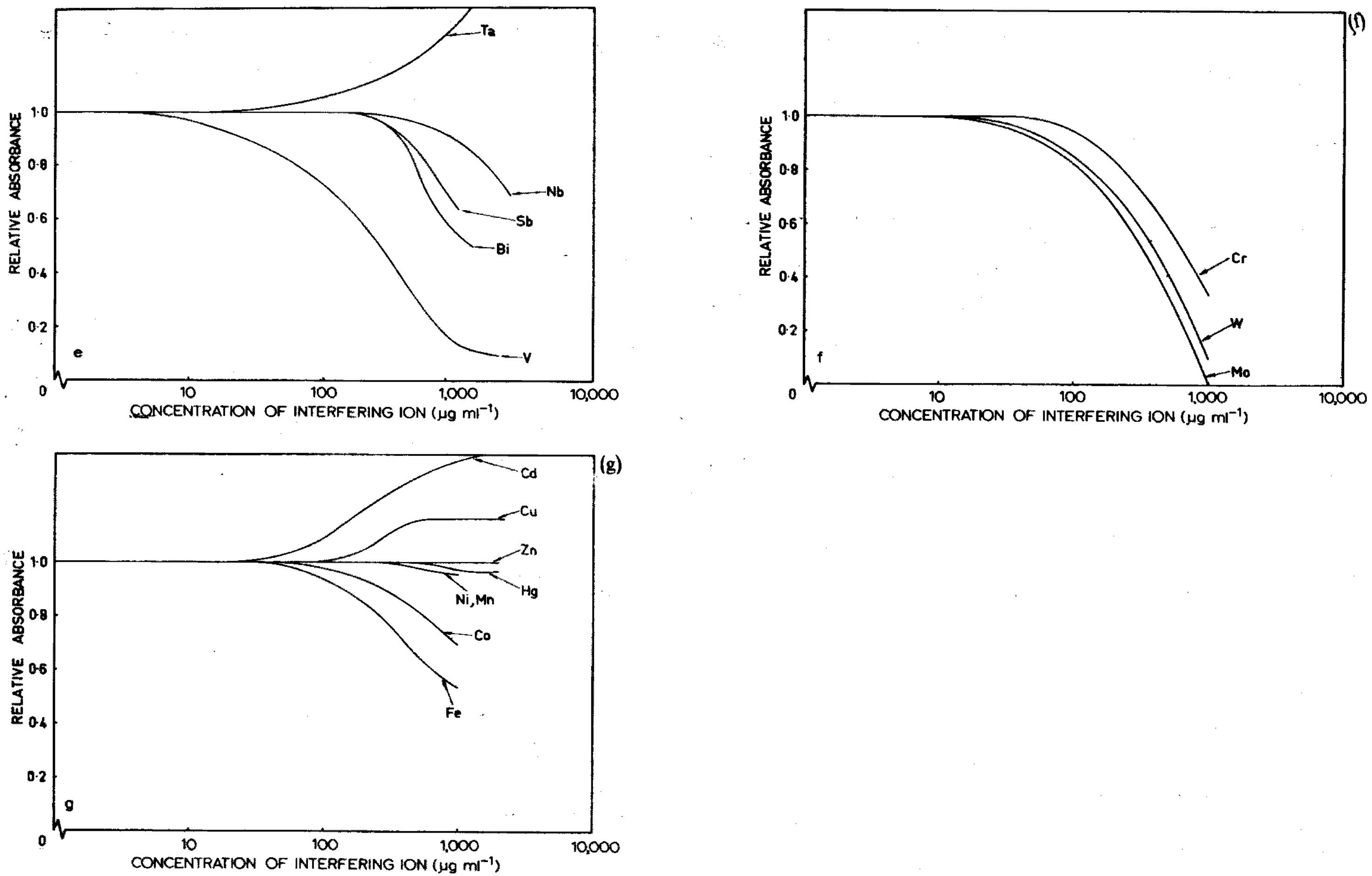

Fig. 3. Effect of various elements on the absorbance of hafnium. (a) Alkali metals; (b) alkaline earth metals; (c) Group III elements; (d) Group IV elements; (e) Group V elements; (f) Group VI elements; (g) various transition elements.

Hafnium

The effects of various acids on the absorption of hafnium were similar to those for zirconium. Sulphuric acid, however, showed a very large depressing effect: 0.5 *M* acid completely suppressed the absorption of 400 μg ml^{-1} hafnium. Acetone and ethanol caused an enhancement, the effect of the latter being about 33% in a 50% mixture with water. Another interesting feature is the observed depression with hydrofluoric acid, in contrast to the behaviour of titanium and zirconium. This observation is, however, not in agreement with that of Amos and Willis[4].

The effects of various metal ions on the absorbances of hafnium (400 μg ml^{-1}) were investigated as for titanium and zirconium.

Figure 3(a) shows the effects of adding alkali elements on the absorbance of hafnium. Lithium had a very large depressing effect whereas the absorbance of hafnium was unchanged in the presence of 1000 μg ml^{-1} cesium. The effects of adding alkaline earth ions are illustrated in Fig. 3(b), the order of depression being Ba > Mg > Ca > Sr. The absorbance of hafnium was completely suppressed by 2000 μg ml^{-1} barium, but the effects of other elements reached a saturation level at this concentration. Figure 3(c) shows the interesting behaviour of Group III elements. These tended to enhance the absorption of hafnium at low concentrations (up to 1000 μg ml^{-1}) but showed a remarkable depressing effect at higher concentrations. The effectiveness of the elements in causing this behaviour appears to be in the order of increasing atomic number, *i.e.* most for boron and least for lanthanum. The effect of adding Group IV elements on the absorbance of hafnium is shown in Fig. 3(d). Tin, lead and titanium at concentrations of about 100 μg ml^{-1} decreased the absorbance, whereas silicon increased it. The effects of Group V elements are shown in Fig. 3(e). Vanadium produced a very marked depression, niobium a somewhat smaller one, and tantalum actually produced an enhancement in the absorbance of hafnium. Bismuth and antimony also had a depressing effect. The effects once again were in the order of the atomic number. The effect of adding group VI and transition elements is shown in Figs. 3(f) and (g). Zinc, manganese, nickel, and mercury did not show much effect, whereas copper and cadmium enhanced the absorption of hafnium. Chromium, molybdenum, tungsten, iron, and cobalt depressed the absorption of hafnium. The effects of the transition metals thus showed many anomalies, though they tended to be periodic in nature.

DISCUSSION

Effects of various reagents

The slight decrease in the absorption of titanium, zirconium, and hafnium by nitric acid can probably be explained by the oxidizing character of the latter which may tend to facilitate the reaction

$$\mathrm{M + O \rightarrow MO} \qquad (1)$$

The enhancement produced by hydrochloric acid may be ascribed to the volatile nature of the chlorides of these metals. Higher concentrations, however, decrease the absorption, because of the increased viscosity of the solutions. Not much can be said about the effects of sulphuric acid but it seems probable that the stabilities and boiling points of the sulphates increase in the order Ti < Zr < Hf. The enhancement of titanium absorption produced by sulphuric acid indicates that titanium sulphate formed in the flame probably decomposes more quickly than the oxide. The enhancement of titanium and zirconium absorption by hydrofluoric acid can be accounted for by the volatile character of the fluorides of these metals[11]. Data could not be obtained on the volatility of hafnium fluoride. The enhancements obtained with organic solvents are most probably due to an increase in the amount of solution reaching the flame[12] and to smaller particle size in the flame[13]. The enhancement observed with ammonia and other nitrogenous compounds has been explained by Bond and Willis[8].

Effects of various ions

The addition of various ions to solutions of titanium, zirconium and hafnium is usually found to enhance the absorption of titanium but depress that of zirconium and hafnium. The effects appear to be periodic in nature and the largest effect is generally produced by the smallest ion. Alkali metals and alkaline earths would be expected to enhance the absorption of elements which are presumably ionized in the flame by acting as ionization suppressors, and the effect would be expected to be greatest with the largest ions. Elements like those of Group IVB have high ionization potentials but in any case the ease of ionization is Hf > Zr > Ti, so that the expected effect of the alkali metals and the alkaline earths is opposite to that actually observed. The explanation for these observations must, therefore, be sought elsewhere.

The presence of the following equilibrium reactions in the flame may be assumed

$$M + O \rightarrow MO \qquad (1)$$

$$M + OH \rightarrow MOH \qquad (2)$$

where M is the atom of titanium, zirconium or hafnium. If X is the atom of the added element the following reactions may also take place

$$X + O \rightarrow XO \qquad (3)$$

$$X + OH \rightarrow XOH \qquad (4)$$

The effects of reactions (3) and (4) on reactions (1) and (2) would be obviously determined by the relative stabilities of the products in the various equilibria. Thus if the products in reactions (3) and (4) are more stable compared with those in reactions (1) and (2), the addition of X would tend to increase the population of M by causing a depletion of O and OH radicals.

The high enhancing effects of lithium and beryllium on titanium support this view. It is further possible, however, that the resulting species in the various equilibria could combine to form association compounds, the stabilities of which would determine the effect of the addition of X on the population of M atoms.

Thus it would appear that the effects of various ions on the absorption of elements like those considered in this work are determined by several complex factors. It appears that ions which form stable hydroxides and oxides cause an enhancement, provided, however, that the various species do not combine with the metal being determined to give stable compounds which are not decomposed at the temperature of the flame. In the latter case, a large depression effect is expected, the magnitude of which is determined by the stability of the compounds formed. It seems that smaller ions generally give rise to more stable compounds with titanium, zirconium and hafnium and, therefore, have a greater effect than larger ions.

CONCLUSIONS

The effects of various ions on the atomic absorption of titanium, zirconium and hafnium appear to be periodic in nature, the smallest ions generally showing the greatest effect. The absorption of titanium is generally increased by adding extraneous ions, except in the case of boron. The absorption of zirconium and hafnium is generally depressed, except with lanthanum, silicon, tantalum, cadmium and copper, where an enhancement is observed.

The author thanks Dr. J. B. Willis for his valuable suggestions and advice. He is also grateful to the staff of Varian Techtron Pty. Ltd. for the help and cooperation received during his tenure of a Colombo Plan Fellowship, and to the Bhabha Atomic Research Centre, Trombay, for leave of absence.

SUMMARY

The effects of various ions and compounds on the atomic absorption signals of titanium, zirconium and hafnium are investigated. The effect appears to be periodic in nature, the smallest ions usually causing the largest effect. The absorption of titanium is usually increased, but that of zirconium and hafnium is generally decreased.

RÉSUMÉ

On examine l'influence de divers ions et composés sur le dosage du titane, zirconium et du hafnium, par absorption atomique. Elle semble de nature périodique: les ions les plus petits ont généralement l'influence la plus grande. L'absorption du titane est ordinairement augmentée, tandis que celles du zirconium et du hafnium sont diminuées.

ZUSAMMENFASSUNG

Der Einfluss verschiedener Ionen und Verbindungen auf die Atomabsorptionssignale von Titan, Zirkon und Hafnium werden untersucht. Die Wirkung scheint periodischer Natur zu sein, die kleinsten Ionen haben gewöhnlich den grössten Einfluss. Die Absorption von Titan wird normalerweise vergrössert, die von Zirkon und Hafnium jedoch verringert.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

AN IMPROVED METHOD FOR THE DETERMINATION OF COBALT IN BIOLOGICAL MATERIALS

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(Received 16th June 1971)

The suggestion of van Klooster[1] that nitroso-R salt (the sodium salt of 1-nitroso-2-naphthol-3,6-disulphonic acid) might be used for the detection of small quantities of cobalt has been very widely exploited; of the methods for estimating trace amounts of cobalt proposed since 1954, more than one third have been based on this compound (Young[2]).

The method developed by Marston and Dewey[3] involved the separation of cobalt from the bulk of other metals present in the acid digests of plant and animal tissue before the final chelation with nitroso-R salt. This was achieved with dithizone in carbon tetrachloride solution, but proved time-consuming and expensive when there was an appreciable excess of extraneous metals. A much less laborious preliminary extraction with 1-nitroso-2-naphthol has been substituted in the modification presented below. This reagent has been extensively used by several investigators[2] for the assay of cobalt and proved particularly effective for the present purpose, where the procedure advocated has been sucessfully employed in this laboratory and elsewhere[5-7]. Improvements in the procedure for digesting organic matter and for eliminating interference from iron(II) are also presented.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Unicam SP 600 spectrophotometer. pH values were determined with a Cambridge pH meter.

Reagents

British Drug Houses A.R. grade chemicals, acids, redistilled solvents and glass-redistilled water were used throughout.

Nitric acid. Distillation from glass, with an effective centrifugal splash head, produced a reagent free from detectable trace metals. During digestion this may conveniently be dispensed from a polythene wash bottle.

Citrate buffer. A 10% (w/v) sodium citrate solution (*ca.* 0.03 *M*) was adjusted to pH 6.8 with 0.05 *M* sulphuric acid and extracted with 1-nitroso-2-naphthol before storage in a refrigerator.

1-*Nitroso*-2-*naphthol.* The reagent was recrystallised twice from petroleum ether. A Soxhlet apparatus was convenient for this purpose. The reagent was stored in the dark under refrigeration. A 0.01 *M* (0.52%) solution in alcohol was used.

Nitroso-R salt. The salt was recrystallised from water. The aqueous 0.2% (w/v) reagent solution was quite stable at room temperature.

Ammonia solution. Distilled water was saturated with ammonia gas from a cylinder.

Standard procedure

Moisten the dried animal or plant material (10–50 g dry weight, or sufficient to provide 1–5 μg cobalt) contained in a 500-ml Kjeldahl flask with water to prevent spontaneous ignition when 10–30 ml of nitric acid is added. Warm the mixture, controlling frothing by vigorous shaking and if necessary by cooling until the initial reaction has subsided.

On cooling, remove any solidified fat, if present in animal tissues, by filtration through a sintered glass funnel, and wash with nitric acid; the removal of excess of fat reduces the risk of subsequent explosive oxidation by perchloric acid (it has been shown that solidified fat does not contain any of the heavy metals). Add 1–3 ml of sulphuric acid, together with two "Pyrex" glass beads, and heat to gentle boiling with further additions of nitric acid from time to time until the solution becomes light-brown. It is then safe to add perchloric acid, drop by drop, alternating with nitric acid, until the digest is colourless. Complete the oxidation by continued heating to fuming point, and leave to fume for 5 min. The digestion may take 4–8 h.

The residual solid material in the digest comprises mainly silicates and alkaline earth sulphates.

Formation of the cobalt–1-nitroso-2-naphthol complex. Boil the completed digest gently with 50 ml of water for 1 min to ensure maximum solution. Then cool, filter through 11-cm Whatman No. 40 paper and wash into a 250-ml conical flask. Add 10–20 ml of citrate buffer and adjust the mixture to pH 4.0 with 20% (w/v) sodium hydroxide solution. If an appreciable amount of iron is present, the remainder of this operation must be carried out in subdued light to limit the photochemical reduction of iron(III) to iron(II)[4].

Heat the solution to boiling, add 3 ml of 1-nitroso-2-naphthol reagent slowly, and boil gently, with the aid of a glass boiling stick, for 3 min. Then add 2 ml of 50% sulphuric acid to the boiling mixture to decompose metal complexes other than that of cobalt. Any iron(II) present appears as a sparingly soluble brown-green complex and is subsequently extracted into chloroform along with the cobalt complex, but may be masked at a later stage by the addition of a few drops of phosphoric acid just before the addition of nitric acid, during the production of the cobalt–nitroso-R salt complex.

Extraction of the complex. Transfer the cooled mixture to a conical 250-ml separatory funnel, rinsing the flask thoroughly with chloroform. Extract 3 times, shaking vigorously, with 5-ml portions of chloroform; this usually suffices for complete extraction. Collect the combined extracts in a suitable boiling tube (200 mm × 22 mm) and remove the excess of solvent carefully by distillation. Oxidize the residue with a few drops each of sulphuric acid and perchloric acid.

Production of cobalt–nitroso-R salt complex. Dilute this digest with a few ml of water and boil for 1 min. Make just alkaline (external indicator) by the addition of ammonia solution and remove the excess of ammonia by boiling. Add 1 ml of citrate buffer and while warm add 1 ml of nitroso-R salt reagent, allowing 5 min for reaction.

Stabilize the complex by boiling with nitric acid (1 ml) for 1 min. Remove the colour of the excess of reagent by adding *ca.* 0.25 ml of aqueous saturated bromine solution while still warm, and standing for 5 min. Then remove excess of bromine by boiling. Do not reduce the volume to less than 7 ml, otherwise some partial decomposition of the complex may occur. Dilute to 10 ml and measure the absorbance at 480 nm in a 1-cm cell against a reagent blank.

RESULTS AND DISCUSSION

Formation of the 1-*nitroso*-2-*naphthol–cobalt complex*

A series of 150-ml sodium citrate (0.03 *M*) solutions containing 25 μg of cobalt at differing pH values was prepared. After the addition of 1-nitroso-2-naphthol reagent (1 ml), complex formation was allowed to proceed for varying times at 100° until the reaction was arrested by the addition of sulphuric acid. Extraction with chloroform and final assay with nitroso-R salt was carried out as described.

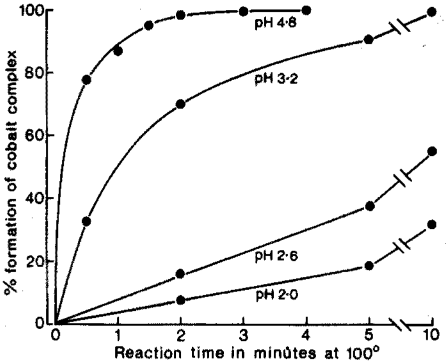

Fig. 1. pH and time dependence of cobalt–1-nitroso-2-naphthol complex formation.

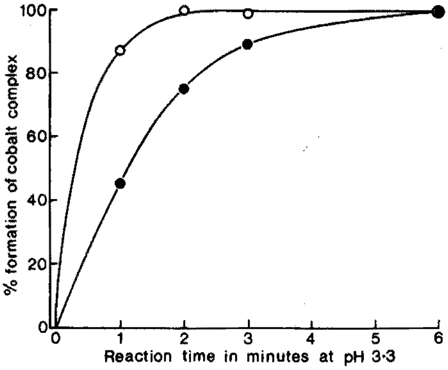

Fig. 2. Effect of 1-nitroso-2-naphthol concentration. 150 ml of citrate buffer (0.03 *M*) containing 25 μg of cobalt adjusted to pH 3.3 was allowed to react with 1-nitroso-2-naphthol reagent at 100°. (●) 1 ml reagent; (○) 2 ml reagent.

The rate of reaction is clearly shown in Fig. 1 to be time- and pH-dependent.

The extent of cobalt complex formation was shown to be directly proportional to the concentration of 1-nitroso-2-naphthol within the pH range 3–5. Raising the pH demonstrably speeded this effect. Acidic conditions were favoured in the preparation of the digest because at higher pH values (*e.g.* above pH 5.0) precipitates of metal hydroxides would be likely to adsorb cobalt ions.

Effect of interfering ions

The effect of interferences and the analytical value of the 1-nitroso-2-naphthol reagent were investigated, to establish the optimal conditions for the extraction procedure of cobalt from acid digests of biological material. The results of this investigation are summarized below.

Citrate buffer solutions (added to prevent hydroxide formation) containing 25 μg of cobalt in the presence of a 200-fold amount of each of the following cations (iron(III), zinc, nickel and copper) were reacted with the reagent at various pH values and reaction times at 100°. When 1 ml of reagent (equivalent to *ca.* 600 μg of cobalt) was used, a 50% suppression of cobalt complex formation occurred over a pH range of 3.3–4.5 in the presence of the metal ion mixture. The addition of 2 ml of reagent under similar conditions allowed 100% formation of the cobalt complex after a 2-min reaction period. Extraction of cobalt was not affected by the presence of even large amounts of the common anions.

The principal interference was from copper and when this was present in amounts greater than 10 mg per sample, its removal was necessary; this could be done conveniently as the sulphide.

The effect of temperature on this system was also studied and it was found that cobalt was preferentially complexed at 100°. The standard conditions for the formation of the 1-nitroso-2-naphthol complex with cobalt contained in biological material therefore involve heating at 100°, because other metals in these materials were found to show an increasing tendency to compete with cobalt at lower temperatures.

Spectrophotometry with nitroso-R salt

For the final spectrophotometric procedure with nitroso-R salt, the calibration curve was found to be linear up to 20 μg of cobalt in the final solution. The absorbance for 20 μg of cobalt was 0.600.

TABLE I

DETERMINATION OF COBALT IN PASTURE RECOVERY EXPERIMENT

(Samples of wheaten hay chaff (20 g) were used for each run)

Co added (*μg*)	*Co found* (*μg*)	*Co content in original sample* (*p.p.m.*)
0	0.8	0.04
0	0.65	0.033
0	0.76	0.038
1	1.6	0.03
3	3.8	0.04
5	5.6	0.03
10	10.6	0.03

A typical recovery of cobalt from biological material is shown in Table I. A similar series was obtained for liver tissue. The cobalt contents of pasture and liver samples were consistent with data obtained from animal experiments[5-7].

SUMMARY

A previously described method for the determination of microgram quantities of cobalt in biological material with diphenylthiocarbazone (dithizone) has been modified to allow the quantitative extraction of cobalt from other metals, with 1-nitroso-2-naphthol as the complexing agent. The effect of reagent concentration and the optimal pH range for the extraction are presented. The determination is completed spectrophotometrically by means of the cobalt–nitroso-R salt complex.

RÉSUMÉ

Une méthode déjà decrite pour le dosage de microquantités de cobalt dans des substances biologiques, à l'aide de dithizone, a été modifiée pour permettre l'extraction quantitative du cobalt d'avec d'autres métaux. On utilise le nitroso-1-naphtol-2 comme réactif complexant. On examine l'influence de la concentration du réactif et du pH sur l'extraction. Le dosage se fait au spectrophotomètre, au moyen du sel complexe cobalt–nitroso-R.

ZUSAMMENFASSUNG

Eine früher beschriebene Methode zur Bestimmung von Mikrogramm-Mengen Kobalt in biologischem Material, bei der Diphenylthiocarbazon (Dithizon) verwendet wird, wurde für die quantitative Extraktionstrennung des Kobalts von anderen Metallen abgewandelt. Hierbei wird 1-Nitroso-2-naphthol als Komplexierungsmittel verwendet. Der Einfluss der Reagenzkonzentration und der optimale pH-Bereich für die Extraktion wurden untersucht. Für die spektrophotometrische Bestimmung wird der Kobalt–Nitroso-R-Salz-Komplex verwendet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN STEELS WITH ARSENAZO III

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(Received 15th April 1971)

Zirconium has been determined spectrophotometrically in steels with arsenazo III in nitric[1], and hydrochloric acids[2,3]. These direct methods can tolerate a maximum of 15 mg of iron and are accurate only when no hydrolytic precipitates or silica are formed during the dissolution procedure. Silica and hydrolytic precipitates formed by tungsten, niobium, tantalum, tin and antimony coprecipitate zirconium to varying degrees. Using xylenol orange as the chromogenic reagent, Cechova[4] found that a direct spectrophotometric procedure cannot be used when hydrolytic precipitates are formed on sample dissolution. The results of a direct method were compared with a phenylarsonic acid separation procedure. After sample dissolution in 4 *M* hydrochloric acid, zirconium was precipitated with phenylarsonic acid, and the precipitate containing hydrolytic precipitates, after filtering and ignition, was fused with potassium hydrogen sulphate. Sulphate interferes with the determination of zirconium with arsenazo III[5] and therefore the phenylarsonic acid procedure for the separation of zirconium cannot be used with this highly sensitive chromogenic reagent.

In the present work, standard steel samples (BCS 273, 275 and 277) containing small amounts of metals which form hydrolytic precipitates were analysed for zirconium by direct dissolution procedures[1,3,4]. This investigation confirmed that without a preliminary separation of zirconium the spectrophotometric results are low.

This paper describes the spectrophotometric determination of zirconium in all types of steels with arsenazo III in 8 *M* hydrochloric acid after a preliminary separation of zirconium with cupferron and iron carrier. The only interference is caused by large amounts of titanium, but with a 0.5-g sample, as little as 2 and 5 p.p.m. of zirconium can be determined in steels containing 1 and 2.5 % of titanium, respectively. Because the zirconium–arsenazo III complex is five times as sensitive as the xylenol orange complex, zirconium in steels can be determined at lower concentrations than reported before.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer with 1-cm glass cuvettes was used.

Standard zirconium solution (100 *μg ml*$^{-1}$). Dissolve 0.3538 g of zirconyl chloride octahydrate in 400 ml of 5 *M* hydrochloric acid, boil for 5 min, cool and dilute to 1 l[5]. Prepare 4 μg ml^{-1} and 10 μg ml^{-1} solutions by suitable dilution with 0.5 *M* hydrochloric acid.

Arsenazo III solution (0.12%). Dissolve 0.12 g of arsenazo III (Aldrich Chem. Co. Inc., U.S.A.) in 100 ml of 0.02 *M* sodium hydroxide.

Recommended procedure

Weigh a 0.5-g steel sample into a 250-ml beaker, add 8 ml of water, 12 ml of 10 *M* hydrochloric acid and 7 ml of 15 *M* nitric acid. After dissolution add 13 ml of 72% perchloric acid and heat until perchloric acid refluxes on the side of the beaker. Cool. Add 50 ml of water, 25 ml of 9 *M* sulphuric acid, 15 ml of saturated sulphur dioxide solution, one accelerator tablet (Whatman, 0.3 g) and boil for 1 min. Cool to *ca.* 12° and add 11 ml of aqueous 8% (w/v) cupferron solution (A.R. grade) from a burette, stirring the solution rapidly. After 15 min filter through a 12.5-cm fast filter paper (Whatman 541). Wash the precipitate twice with 20 ml of 1 *M* hydrochloric acid.

Transfer the precipitate to a 50-ml platinum crucible, place in a muffle furnace and ignite at 700° for 30 min. Cool. Cover with 2 g of sodium peroxide powder (B.D.H. Micro-analytical reagent) and heat in a muffle furnace at 580° for 30 min. Cool. Dissolve the melt in a Teflon beaker containing 80 ml of water. Wash the platinum crucible with *ca.* 20 ml of water and boil the solution for 5 min. Cool. Filter through a 9-cm medium filter paper (Whatman 540). Return the precipitate and filter paper to the Teflon beaker, add 35 ml of 8 *M* hydrochloric acid and boil for 1 min. Cool. Filter the solution through a 7-cm fast filter paper (Whatman 541) into a 50-ml volumetric flask. Wash the beaker and filter paper with 8 *M* hydrochloric acid until the volume in the flask reaches the mark. Mix.

Transfer an aliquot (25 ml or less) containing 15–25 μg of zirconium and not more than 2.5 mg of titanium into a 50-ml volumetric flask (10 ml of solution contains 7.5 ml of 10 *M* hydrochloric acid). Add 10 *M* hydrochloric acid to increase the total amount of 10 *M* hydrochloric acid to 40 ml. Add 0.5 ml of 2% ascorbic acid (freshly prepared) and mix. Cool in ice-water below ambient temperature, add 3 ml of arsenazo III solution, dilute to volume and mix. Measure the absorbance against a blank at 665 nm in a 1-cm cell.

Prepare a standard and a blank by taking 0.5 g of pure iron through the whole procedure with and without the addition of 100 μg of zirconium.

DISCUSSION

Dissolution of sample

The samples are dissolved in a dilute nitric–hydrochloric acid mixture in glass beakers followed by fuming with perchloric acid. Hydrofluoric acid cannot be used because fluoride attacks glass, thus introducing zirconium impurity from the dissolved glass. Addition of 1 ml of 40% hydrofluoric acid will introduce *ca.* 100 μg of zirconium from Pyrex beakers. Samples were also dissolved in Teflon beakers with the addition of hydrofluoric acid, but zirconium results did not differ from those obtained by dissolution in glass beakers. It is considered better to retain silica in the solution using the precipitated silica as a scavenger for small amounts of zirconium.

Sensitivity and stability of the method

The zirconium–arsenazo III complex, when measured against the blank in

8 *M* hydrochloric acid has maximum absorbance at 665 nm. The molar absorptivity of the complex is $1.41 \cdot 10^5$, corresponding to 0.0064 μg Zr cm^{-2} on the Sandell scale. Ascorbic acid is added to reduce any oxidising agents formed during the dissolution of iron hydroxide in 8 *M* hydrochloric acid. Solutions prepared for spectrophotometric determination must be cooled below ambient temperature to counteract the heat produced on diluting strong hydrochloric acid with water. The solutions are stable for at least 30 min[5].

Recovery of zirconium and precipitation with cupferron

The recovery of zirconium by the recommended procedure is 97%, and depends on the amount of iron coprecipitated with zirconium. In all recovery experiments, 100 μg of zirconium was added to plain or alloy steels at the beginning of the dissolution. The solution for the precipitation of zirconium with cupferron was 1 *M* in perchloric acid and 2.25 *M* in sulphuric acid. An acid mixture 1 *M* in perchloric and hydrochloric acids was investigated, but chromium was partially precipitated and the amount of iron precipitated by cupferron was lower than when perchloric–sulphuric acid mixture was used. After the addition of 11 ml of 8% cupferron the precipitate contained *ca.* 72 mg of iron for sample sizes of 0.25–0.5 g, giving a maximum recovery of 97% (Fig. 1). A 0.1-g steel sample gave only 95% recovery. When impure cupferron is used, sufficient reagent must be added to precipitate between 70 and 75 mg of iron. When the amount of iron in the steel sample falls below 250 mg, the iron should be increased to 500 mg with iron(III) chloride solution.

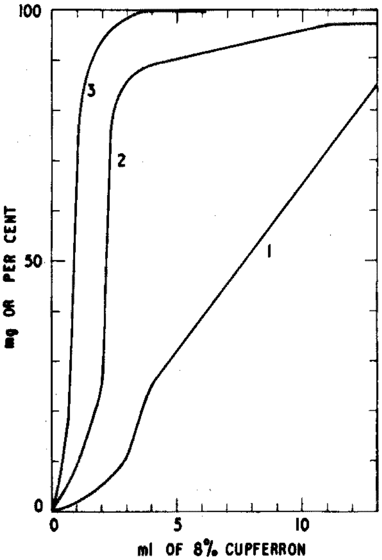

Fig. 1. The precipitation of iron, zirconium and titanium with cupferron. (1) Amount of iron in mg precipitated by cupferron; (2) percentage recovery of zirconium by the recommended procedure; (3) percentage recovery of zirconium and titanium in the cupferron precipitate.

Although 4 ml of 8% cupferron will precipitate all the zirconium, and about 24 mg of iron, for maximum recovery of zirconium 72 mg of iron is required in the precipitation stage after sodium peroxide fusion. The sodium hydroxide concentration, the volume of water, and the iron(III) concentration are related. It was found that when 2 g of sodium peroxide was used for the fusion, 100 ml of water and 72 mg of iron(III) were required to retain the maximum amount of zirconium. Smaller or larger volumes of water produced lower zirconium recoveries. An increase in the iron content above 72 mg did not produce higher recoveries.

Fusion with sodium peroxide

Various mixing techniques were tried for fusion of the ignited cupferron precipitate with sodium peroxide. In the case of sample SRM 1162, the maximum result was obtained only when the sample was covered with 2 g of sodium peroxide, while mixing and subsequent covering with sodium peroxide gave low results. Therefore, the ignited precipitate must be covered with 2 g of sodium peroxide. Although 50-ml platinum crucibles are recommended for the ignition of the cupferron precipitate, 25-ml crucibles can be used, but the cupferron precipitate takes longer to ignite. The loss of platinum per fusion is approximately 5 mg which is not excessive compared with the loss of platinum after fusion with sodium tetraborate (2 g of sodium tetraborate dissolve 3 mg of platinum in 30 min).

Dissolution of zirconium–iron hydroxides

It is known that high acid concentrations are required to depolymerize zirconium[5]. The best zirconium results were obtained when the iron(III) precipitate was dissolved in 35 ml of 8 *M* hydrochloric acid and boiled for 1 min. During the dissolution some hydrochloric acid was lost and the final acidity of 7.5 *M* was obtained after filtration and dilution with 8 *M* hydrochloric acid to 50 ml.

Blanks and standard curve

Blanks which were taken through the whole procedure and contained iron were almost identical with blanks prepared directly from water. Once the percentage recovery of zirconium has been established, a standard curve incorporating the recovery factor may be used for the determination of zirconium in steels. In the direct method, 20 μg of zirconium in 50 ml of 8 *M* hydrochloric acid produced an absorbance of 0.620 and an absorbance of 0.601 was used to calculate the zirconium in samples.

Effect of various metals

It was found that during the dissolution of the sodium peroxide melt some metals which form soluble sodium salts were partially adsorbed by iron(III) hydroxide. Only traces of molybdenum and tungsten could be found in the final 7.5 *M* hydrochloric acid solution, but all the titanium and 20% of the niobium were retained by the iron(III) hydroxide. No interference was noticed in the spectrophotometric determination of zirconium when 3% niobium steel was analysed by the recommended procedure. Iron(III) interfered slightly in the spectrophotometric procedure, but even for 25-ml aliquots the error was only 0.1 μg (36 mg iron(III) $\equiv$ 0.004 absorbance).

Titanium interfered either by producing colours with arsenazo III in solutions which were higher than 8 *M* in hydrochloric acid, or by giving lower absorbances in less concentrated hydrochloric acid. In 8 *M* hydrochloric acid the amount of titanium in a sample aliquot for spectrophotometric determination was limited to 2.5 mg;

higher amounts of titanium produced lower results. It is also important that in the presence of titanium the ascorbic acid be added after the addition of 40 ml of 10 *M* hydrochloric acid to the sample aliquot. When ascorbic acid was added to weak hydrochloric acid solutions containing titanium, more than 1 mg of titanium produced lower absorbances.

Correction for thorium

Although thorium is unlikely to be present in steels, nevertheless even trace amounts of thorium interfere seriously in the spectrophotometric determination of zirconium; 1 μg of Th gives a positive error equivalent to 0.34 μg of Zr. A check for thorium can be made in the final 50-ml sample solution, on the basis that oxalate complexes zirconium in 3.6 *M* hydrochloric acid[6]. The method is as follows.

Procedure. Pipette an aliquot (7.5 *M* in hydrochloric acid) containing 0–80 μg

TABLE I

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN STEELS

Sample	*Certified Zr* (%)	*Zr found* (%)
BCS 273 (mild steel)	Trace	0.0019
		0.0001[a]
		0.0013[c]
BCS 275 (mild steel)	0.015	0.0172
		0.0129[a]
		0.0040[b]
		0.0002[c]
BCS 277 (mild steel)	0.040	0.0465
		0.044[d]
		0.0400[a]
		0.0360[b]
		0.0250[c]
BCS 235/1 (18/8 stainless steel + Ti)	—	0.0012
BCS 312 (13Ni–24Co + Ti and Nb)	—	0.0082
BCS 220/1 (7W–5Mo)	—	0.0250
BCS 241/1 (20W–5Cr–V–Mo)	—	0.0246[e]
SRM 1161 (low alloy steel)	< 0.005	0.0015
SRM 1162 (low alloy steel)	0.063	0.0589
		0.0580[f]
SRM 1163 (low alloy steel)	0.20	0.188[e]
SRM 1164 (low alloy steel)	0.010	0.0090
SRM 1165 (ingot iron)	0.002	0.0007
SRM 1166 (ingot iron)	< 0.005	0.0012
SRM 1167 (low alloy steel)	0.094	0.0890
		0.0900[f]
SRM 1168 (low alloy steel)	< 0.005	0.0002

[a] Dissolved as in Ref. 1.

[b] Dissolved as in Ref. 2.

[c] Direct dissolution in 4 *M* HCl as in Ref. 4.

[d] Ref. 4, separation with phenylarsonic acid.

[e] 0.25-g sample. Added 250 mg Fe as $FeCl_3$.

[f] Separated with phenylarsonic acid as in Ref. 4.

of thorium and not more than 10 mg of iron, 500 μg of titanium and 75 μg of zirconium into a 50-ml volumetric flask. Add 5 ml of water, 1 ml of 1% ascorbic acid and 7.5 *M* hydrochloric acid to obtain a total volume of 24 ml of 7.5 *M* hydrochloric acid. Add 10 ml of 8% oxalic acid solution and cool to room temperature. Add 3 ml of 0.25% arsenazo III solution, dilute to volume and mix. Measure the absorbance at 660 nm in 1-cm cell against a reagent blank.

Separation methods vs. *direct determination*

The results obtained for a variety of steels are shown in Table I. The zirconium results for BCS 273, 275 and 277 steels, which contain small amounts of metals forming hydrolytic precipitates, are compared with results obtained by direct dissolution methods. The zirconium results obtained by direct dissolution are low and depend on the amount of the hydrolytic precipitate formed during the various dissolution procedures.

As more and more scrap is returned to steelmaking processes there is a greater possibility of introducing small amounts of metals which form hydrolytic precipitates which after dissolution would retain varying amounts of zirconium. The only means of overcoming this problem is to use a separation method. The advantage of using arsenazo III as a chromogenic reagent for the determination of zirconium is the high molar absorptivity ($1.4 \cdot 10^5$). Whereas the SRM certificate gives the lowest zirconium values as less than 0.0050%, the proposed method can determine zirconium as low as 0.0002% in steels containing less than 1% of titanium.

In addition this method provides a relatively fast separation procedure, and 6 samples can easily be determined in 8 h.

Reproducibility of the method

The recovery of zirconium, provided that between 70 and 75 mg of iron were coprecipitated with cupferron, was between 96.5 and 97.5% with the majority of recoveries being at 97%.

Determination of titanium

Although new and more sensitive chromogenic reagents[7,8] have been proposed for the determination of titanium, the spectrophotometric determination of titanium as its peroxide complex is still widely used. Existing methods recommend that steel samples be dissolved in non-oxidising acids and titanium separated as the cupferron complex from the major matrix elements. After ignition and fusion with potassium hydrogen sulphate titanium is determined as the yellow titanium–peroxide complex. This procedure works very well for plain carbon steels, but for nickel–chromium alloy steels[9] a lengthy cyanide–8-hydroxyquinoline–cupferron separation method must be used. This proposed method provides a fast and simple separation procedure of titanium from stainless steels.

The precipitation of titanium with cupferron from solutions used for the separation of zirconium was investigated. It was found that as with zirconium, 4 ml of 8% cupferron will precipitate all the titanium (Fig. 1). After ignition and fusion with potassium hydrogen sulphate the titanium–peroxide complex was developed in the usual manner in 3.5 *N* sulphuric acid to overcome the effect of alkali metal sulphates. The absorbance was measured at 450 nm where there is no interference by molybdenum, niobium or vanadium, which are coprecipitated to a varying degree by cupferron.

It is a pleasure to acknowledge the assistance given by Miss J. R. Kennedy with the experimental work.

SUMMARY

A general method is presented for the spectrophotometric determination of zirconium in steels with arsenazo III. Steel samples are dissolved by fuming with perchloric acid and zirconium is separated with cupferron, iron being used as carrier. The only interference is caused by titanium, but as little as 2 and 5 p.p.m. of zirconium can be determined in steels containing 1 and 2.5 % of titanium, respectively. Titanium can also be separated with cupferron and subsequently determined as the yellow titanium–peroxide complex.

RÉSUMÉ

Une méthode générale est proposée pour le dosage du zirconium dans les aciers, à l'aide d'arsènazo III. Les échantillons d'acier sont dissous dans l'acide perchlorique; le zirconium est séparé à l'aide de cupferron, en utillisant le fer comme entraîneur. La seule interférence est causée par le titane; cependant il est possible de doser 2 et 5 p.p.m. de zirconium dans des aciers renfermant 1 à 2.5% de titane, respectivement. Le titane peut également être séparé à l'aide de cupferron et dosé ensuite sous forme du complexe jaune titane–peroxyde.

ZUSAMMENFASSUNG

Es wird eine allgemeine Methode für die spektrophotometrische Bestimmung von Zirkonium in Stählen unter Verwendung von Arsenazo III vorgelegt. Die Stahlproben werden durch Abrauchen mit Perchlorsäure aufgelöst, und das Zirkonium wird mit Kupferron abgetrennt, wobei Eisen als Träger dient. Die einzige Störung wird durch Titan hervorgerufen, jedoch können so geringe Gehalte wie 2 und 5 p.p.m. Zirkonium in Stählen mit 1 bzw. 2.5 % Titan bestimmt werden. Titan kann ebenfalls mit Kupferron abgetrennt und danach als gelber Titan–Peroxid-Komplex bestimmt werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

STUDIES WITH DITHIZONE

PART XXVII. PRIMARY COPPER(I) DITHIZONATE

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(Received 23rd June 1971)

Although the reaction between copper(II) and dithizone (3-mercapto-1,5-diphenylformazan; H_2Dz) has been investigated by several authors[1-4], the literature contains fewer and somewhat contradictory data concerning the reactions of copper(I). This may be due to the limited analytical applications of the copper(I) complexes or to experimental difficulties inherent in the solution chemistry of copper(I) whose soluble compounds are often sensitive to aerial oxidation or disproportionate into copper(II) and metallic copper.

According to Sandell[5], copper(I) reacts with dithizone in acidic and alkaline solutions to give violet primary and yellow-brown secondary complexes, respectively. Welcher[6] states that the complex formed under acidic conditions is red-brown to violet while the other is greenish brown and probably a compound of copper(II). Koroleff[3] showed that copper(I) (as copper(I) chloride in 0.1 *M* hydrochloric acid containing hydroxylamine) gave a brown complex with no violet nuance, which was a 1:1 complex of formula CuDz. The violet secondary complex formed on shaking with ammonia was insoluble in carbon tetrachloride. The formula Cu_2Dz was proposed although no analysis was carried out*.

Quite recently Freiser and Freiser [7] claimed that secondary copper(II) dithizonate was actually a mixture of primary copper(I) dithizonate and an oxidation product of dithizone, *viz.* diphenylthiocarbadiazone (DTD) formed as a result of a redox reaction

$$2Cu^{2+} + 3H_2Dz \rightarrow 2Cu(HDz) + DTD \qquad (1)$$

It has been shown elsewhere[8] that this suggestion is at variance with experimental data. During these studies it was necessary to show that primary copper(I) dithizonate could be clearly distinguished from primary and secondary copper(II) dithizonate, and identified in admixtures with these complexes or dithizone. The present paper describes a study of the formation of the copper(I) complex and some of its reactions.

EXPERIMENTAL

Reagents

Dithizone, chloroform and aqueous solutions of buffers were purified as

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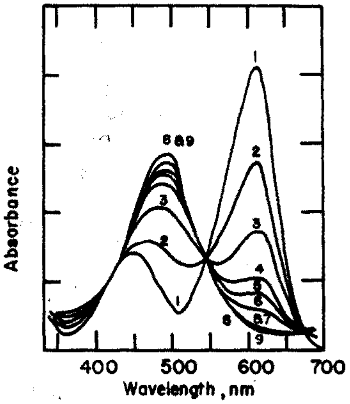
* Koroleff[3] used the symbol HDz for dithizone but he used the same symbol Dz for both the uninegative anion (our HDz^-) and for the further deprotonated anion which we formulate as Dz^{2-}.

described in earlier papers of this series. The customary precautions were used in cleaning glassware for use with dithizone. Absorptiometric measurements were carried out in matched 1-cm silica cells with Unicam SP 500 and SP 700 spectrophotometers.

Unless otherwise stated, solutions of copper(I) were freshly prepared by mixing solutions of copper(II) sulphate of known concentration with an excess of hydroxyammonium chloride, so that the final solution was 1 *M* with respect to chloride.

The reaction between dithizone and copper(I)

A series of mixtures comprising 10 ml of a $1.01 \cdot 10^{-5}$ *M* solution of dithizone in chloroform, *x* ml of copper(II) sulphate ($3.0 \cdot 10^{-5}$ *M*) in 1.0 *M* hydroxyammonium chloride, and $(10-x)$ ml of 1 *M* hydroxyammonium chloride ($x=1.0$, 2.0, 2.5, 3.0, 3.5, 5.0, 7.0, 9.0) at *ca.* pH 3.5 were shaken mechanically for 5 min. The phases were separated and the spectra of the organic layer measured (Fig. 1).



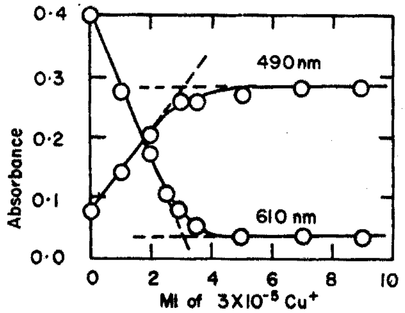


Fig. 1. The absorption spectrum of the organic phase obtained by equilibrating dithizone in chloroform with an aqueous phase containing copper(I), as described in the text. Spectra 1–9 correspond consecutively to the *x* values listed in the text.

Fig. 2. The absorbance at 490 and 610 nm of the organic phases obtained in the experiments shown in Fig. 1 plotted against the volume *x* of copper solution.

The stoicheiometry of primary copper (I) dithizonate

Absorbances of the above organic phases were measured at 490 and 610 nm with a Unicam SP 500 spectrophotometer and are shown plotted against *x*, the volume of copper(I) solution, in Fig. 2; 10 ml of $1.01 \cdot 10^{-5}$ *M* dithizone has reacted with 3.2 ml of $3.0 \cdot 10^{-5}$ *M* copper(I), leading to the ratio $[Cu]:[H_2Dz]=1:1.05$ and the formula $Cu(HDz)$.

The molar absorptivity of primary copper(I) dithizonate

A highly purified solution of dithizone in chloroform (peak ratio $A_{610}/A_{440}=2.48$) was completely converted into copper(I) dithizonate by equilibration with a slight excess of copper(I) in hydroxyammonium chloride (1.0 *M*; pH 3.4). After phase separation, the absorbance of the organic layer was measured at $\lambda_{max}=490$ nm.

Four different samples of dithizone were used.

Initial dithizone

Wavelength	*Absorbance, A, of sample*			
610 nm	0.812	0.613	0.410	0.205
440 nm	0.325	0.248	0.165	0.082
490 nm	0.185	0.135	0.095	0.048
$A_{610}/A_{440}=2.48$				

Resulting copper(I) complex

490 nm	0.568	0.424	0.285	0.141
$\varepsilon_{\max}$calc.	28,100	28,200	27,800	28,000
	Average $\varepsilon_{490}=28.0\ (\pm 0.2)\cdot 10^3$			

This calculation assumes the value $\varepsilon_{610}=40{,}000$ for dithizone.

The effect of pH on the extractability of copper(I) dithizonate

Aliquot portions (10 ml) of a solution of purified dithizone in chloroform ($1\cdot 10^{-5}$ *M*) were equilibrated with equal volumes of copper (I) solution ($3\cdot 10^{-6}$ *M*) in 1 *M* hydroxyammonium chloride of various pH values by shaking for 5 min in stoppered Pyrex test tubes. After phase separation, the organic layer was removed and its absorbance measured at 490 nm (where preliminary measurements had shown the absorption of the copper(I) chelate to be maximal) and at 610 nm (where the absorption of unreacted dithizone is greatest while that due to the copper complex is very small). The percentage of copper extracted was calculated from the absorbance at 490 nm after subtracting the contribution due to unreacted dithizone

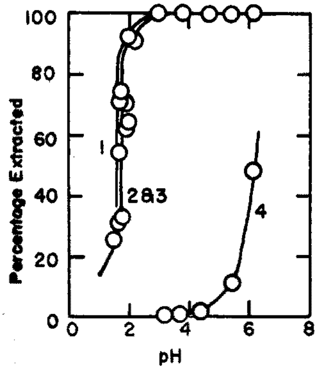


Fig. 3. The effect of pH on the extraction of copper(I) dithizonate into chloroform. (1) 0.5 *M* hydroxyammonium chloride + 0.5 *M* sodium perchlorate; (2) 1.0 *M* hydroxyammonium chloride; (3) 0.8 *M* hydroxyammonium chloride + 0.133 *M* hydroxyammonium sulphate; (4) 0.5 *M* hydroxyammonium chloride and 0.133 *M* sodium thiosulphate.

by using the relationship $A_{490}/A_{610}=0.229$. The pH of the aqueous phase was measured after equilibration.

In view of the possibility that anions in the aqueous phase could complex copper(I) and so reduce the percentage extraction, similar measurements were carried out from aqueous solutions containing 0.5 *M* sodium perchlorate with 0.5 *M* hydroxyammonium chloride ($I=1.0$), 1.0 *M* hydroxyammonium chloride ($I=1.0$), 0.8 *M* hydroxyammonium chloride and 0.133 *M* hydroxyammonium sulphate ($I=1.2$) and 0.5 *M* hydroxyammonium chloride and 0.133 *M* sodium thiosulphate ($I=1.5$). The results are shown in Fig. 3.

DISCUSSION

The above experiments show that the reaction between a weakly acidic aqueous solution of copper(I) with one of dithizone in chloroform leads to equilibrium with a single new species (*cf.* Fig. 1; isosbestic points at 420, 445 and 678 nm), which is shown to be the 1:1 complex Cu(HDz) (Fig. 2) in agreement with the result arrived at by Koroleff[3] using a different method.

$$Cu^+ + (H_2Dz)_{org} \overset{K_{ex}}{\rightleftharpoons} Cu(HDz)_{org} + H^+ \qquad (2)$$

Unlike the equilibrium between copper(II) and dithizone leading to primary copper(II) dithizonate which often requires as much as 30 min, the corresponding equilibrium with copper(I) is established fairly quickly (*ca.* 3 min). The same complex is formed by shaking an aqueous solution of bis(ethylenethiourea)copper(I) chloride with one of dithizone in chloroform. When the corresponding complex of thiourea with copper(I) chloride is used a mixture of copper(I) and copper(II) dithizonates resulted.

The orange-brown colour of the complex ($\lambda_{max}=490$ nm, $\varepsilon_{max}=(28.0\pm0.2)\cdot10^3$ in chloroform; $\lambda_{max}=480$ nm, $\varepsilon_{max}=(21.3\pm0.3)\cdot10^3$ in carbon tetrachloride) agrees with that reported by Koroleff[3], but the wavelength of maximum absorbance is higher than that reported by Freiser and Freiser[7] (*viz.* 478 nm in chloroform) and no evidence was found for the violet colour reported by Sandell[5].

Solutions of primary copper(I) dithizonate in chloroform are stable for at least 30 min at room temperature even when exposed to diffuse daylight (Table I) in a stoppered cell.

The percentage of copper(I) extracted as its primary dithizonate is a function of the pH and reagent concentration (*cf.* eqn. 1) and also depends on the nature of the ions present in the aqueous phase. As shown in Fig. 3, the extraction increases with pH and the percentage extracted at any given pH is found to decrease in the order perchlorate > sulphate > chloride > iodide > thiosulphate, an order which reflects an increasing tendency to form water-soluble copper(I) complexes.

TABLE I

STABILITY OF SOLUTIONS OF COPPER(I) DITHIZONATE IN CHLOROFORM AT *ca.* 16° IN DIFFUSE DAYLIGHT

Time (min)	5	15	30	45	60	90	150
Absorbance, 490 nm	0.320	0.320	0.318	0.315	0.312	0.306	0.300

TABLE II

EXTRACTION DATA OF COPPER(I) DITHIZONATE FROM VARIOUS AQUEOUS SOLUTIONS INTO CHLOROFORM

Composition of aq. phase	*pH-range for complete extraction*	*Conditional extraction constant, log K'*
1. 0.5 *M* Hydroxyammonium chloride + 0.5 *M* $NaClO_4$	2.7–6.5	3.63
2. 0.8 *M* Hydroxyammonium chloride + 0.133 *M* Hydroxyammonium sulphate	2.8–6.5	3.44
3. 1.0 *M* Hydroxyammonium chloride	2.8–6.5	3.44
4. 0.5 *M* Hydroxyammonium chloride + 0.133 *M* $Na_2S_2O_3$	Incomplete extraction	−0.85

TABLE III

THE EXTRACTION OF COPPER(I) FROM SOLUTIONS CONTAINING VARYING AMOUNTS OF CHLORIDE ION[a]

(10 ml of $3\cdot10^{-6}$ *M* copper (I) solution of constant pH and ionic strength ($I=3.25$ *M*) extracted by an equal volume of $1.125\cdot10^{-5}$ *M* dithizone in chloroform)

$[Cl^-]_{tot}$	$[ClO_4^-]$	*pH*	*q*	*log K'*	*log X*
0.25	3.00	2.41	Partial oxidation		4.9
0.85	2.40	2.36	V. large	—	6.1
1.25	2.00	2.37	4.30	3.30	6.55
1.85	1.40	2.39	1.24	2.71	6.96
2.65	0.60	2.38	0.31	2.08	7.39
3.25	0.00	2.42	0.15	1.71	7.61

[a] The ratios $A_{610}/A_{440}=2.50$ and $A_{490}/A_{610}=0.205$ were used in the calculations.

Table II summarises the pH ranges for maximum extraction of the copper(I)–dithizone complex from aqueous solutions containing various anions, together with the experimentally determined distribution ratio, *q*, and the conditional extraction constants, *K'*, defined as follows:

$$K' = \frac{[\mathrm{Cu(HDz)}]_{\mathrm{org}}[\mathrm{H}^+]}{\Sigma[\mathrm{Cu}^+][\mathrm{H_2Dz}]_{\mathrm{org}}} = q\frac{[\mathrm{H}^+]}{[\mathrm{H_2Dz}]_{\mathrm{org}}} \tag{3}$$

The effect of chloride ion as a masking agent was further studied by measuring the values of *q* and *K'* with aqueous solutions of constant pH and ionic strength $I=3.25$ *M* obtained from admixtures of sodium chloride and sodium perchlorate. The results given in Table III show that there is a danger of oxidation to copper(II), unless the concentration of chloride ion is sufficient to stabilise copper(I).

Since the total concentration of copper(I) in the aqueous phase may be expressed in the form

$$\Sigma[\mathrm{Cu}^+] = \Sigma[\mathrm{CuCl}_n]^{1-n} = [\mathrm{Cu}^+]\sum_0 \beta_n[\mathrm{Cl}^-]^n \tag{4}$$

eqn. (2) can be rewritten in the form

$$K' = K_{ex}/X$$
$$\text{or } \log K' = \log K_{ex} - \log X \qquad (5)$$

where K_{ex} is the equilibrium constant of eqn. (2), and $X = \Sigma_0 \beta_n[Cl^-]^n$. Values of the function X for complexes of copper(I) and chloride ions have recently been measured[9] at 25° in a medium containing 0.1 M acid with an ionic strength maintained at $I = 5\ M$ by the addition of sodium perchlorate. The species $CuCl_2^-$ and $CuCl_3^{2-}$ predominate with overall stability constants $\beta_2 = 1.00 \cdot 10^6$ and $0.97 \cdot 10^6$, and there is evidence for the dimer $Cu_2Cl_4^{2-}$ ($\beta_{24} = 1.2 \cdot 10^{13}$), whereas the species $CuCl_4^{3-}$ is not found with $[Cl^-] < 2.5\ M$.

From a large-scale plot of data for log X against $[Cl^-]$, values of log X were interpolated for each chloride ion concentration used in the distribution experiments (Table III) and the plot of log K' against log X (not reproduced) was a straight line of equation:

$$\log K' = 13.07 - 1.49 \log X$$

leading to the value $\log K_{ex} = 13.07$, when log X (and hence $[Cl^-]) = 0$. However, the slope of unity predicted by eqn. (5) was not found. Whether this is due to the use of values of log X appropriate to solutions of ionic strength 5 M whereas our own measurements refer to $I = 3.25\ M$, or whether the neglect of the species $Cu_2Cl_4^{2-}$ is significant, can only be decided after much more extensive measurements of partition equilibria, preferably by using radioactive copper tracer for measurements of q which would then be independent of any assumptions as to the composition and molecular absorptivity of the extractable species.

In many experiments carried out with aqueous phases of different compositions, it was found that partial oxidation of copper(I) to copper(II) (and the consequent extraction of a mixture of the dithizonates Cu(HDz) and $Cu(HDz)_2$) was likely to occur if, for a given concentration of hydroxyammonium ions as reductant, any substantial excess of chloride ions was replaced by perchlorate or sulphate ions. This is explicable by the low stability of the complex species CuCl ($\beta_1 \cong 500$) so that perceptible amounts of copper(II) are formed as soon as $\bar{n}$ falls significantly below 2 (*i.e.* for $[Cl^-] < 0.1\ M$) and its disproportionation will lead to copper(II).

The effect of sulphate ions was investigated by extraction experiments carried out at pH 2.26 and $I = 3.25$. As shown in Table IV, the percentage extraction is very slightly increased on replacing sodium chloride by an equivalent amount of ammonium sulphate showing that chloride ions form stronger complexes. The low extraction from aqueous phases containing thiosulphate ions (Fig. 3) reflects their known tendency to form stable complex anions with copper(I) (*e.g.* $\beta_2 \cong 10^{12}$, $\beta_3 = 10^{9.9}$, $\beta_4 = 10^{10.1}$ etc. at 20°). Strong complexes are also formed by iodide ions ($\beta_2 = 10^5$ at 19°) and especially by cyanide ions ($\beta_2 = 10^{21.7}$, $\beta_3 = 10^{26.3}$, $\beta_4 = 10^{28.6}$ at 20°), so that solutions of primary copper(I) dithizonate are completely reverted to dithizone and water-soluble copper(I) complexes on shaking with 1 M sodium thiosulphate or potassium cyanide or 3 M potassium iodide. Sodium chloride, bromide, sulphate or perchlorate have no such effect.

When reduction was attempted in the absence of chloride ions by using hydroxyammonium sulphate only, the results were inconsistent, doubtless because of the

TABLE IV

THE EFFECT OF SULPHATE ON THE EXTRACTION OF COPPER(I)

(10 ml of a $3 \cdot 10^{-6}$ *M* copper(I) solution containing hydroxyammonium chloride, sodium perchlorate and ammonium sulphate at pH 2.26 and constant ionic strength $I = 3.25$ *M* was extracted by an equal volume of $1.16 \cdot 10^{-5}$ *M* dithizone in chloroform)

$[Cl^-]$	$[ClO_4^-]$	$[SO_4^{2-}]$	A_{610}	A_{490}	*A complex only, calc.*	*% Extraction*
1.15	2.10	0.00	0.382	0.180	0.104	Partial oxidation to Cu(II)
2.10	1.15	0.00	0.432	0.155	0.068	81
1.15	0.00	0.70	0.390	0.153	0.075	90

ease of disproportionation of uncomplexed copper(I) and the simultaneous extraction of dithizonates of copper(I) and copper(II); the addition of copper turnings sometimes made it possible to achieve quantitative extraction of the initial copper(II) as copper(I) dithizonate.

The pH of extraction must be below 6.5, for in more alkaline solution there is an increasing danger of reoxidation to copper(II). If the aqueous phase is made alkaline with sodium hydroxide, copper(I) is speedily oxidised and secondary copper(II) dithizonate is extracted. If, however, the reduced solution is made alkaline with ammonia an unstable magenta complex (λ_{max} 516 nm; ε_{max} 19,000) is formed. This may be the 'secondary copper(I) dithizonate' reported by Koroleff[3] and Sandell[5].

Although the above experiments confirm the stoicheiometry of extractable primary copper(I) dithizonate as $[Cu]:[H_2Dz] = 1:1$, the structure of this complex remains undetermined. The effect of complexing anions on the position of equilibrium and on the rate of attaining equilibrium is certainly complex and, while there is now no doubt as to the existence of this complex, it can clearly play no immediate role in quantitative analytical chemistry.

SUMMARY

The conditions under which copper(I) can be extracted by dithizone (H_2Dz) have been investigated and the composition of the orange-brown primary dithizonate is shown to be Cu(HDz), with $\lambda_{max} = 490$ nm, $\varepsilon_{max} = (28.0 \pm 0.2) \cdot 10^3$ in chloroform and $\lambda_{max} = 480$ nm, $\varepsilon_{max} = (21.3 \pm 0.3) \cdot 10^3$ in carbon tetrachloride. Some of its reactions are reported.

RÉSUMÉ

Une étude est effectuée sur les conditions d'extraction du cuivre(I) par la dithizone (H_2Dz). La composition du dithizonate primaire brun orange est Cu(HDz) avec $\lambda_{max} = 490$ nm, $\varepsilon_{max} = (28.0 \pm 0.2) \cdot 10^3$ dans le chloroforme et $\lambda_{max} = 480$ nm, $\varepsilon_{max} = (21.3 \pm 0.3) \cdot 10^3$ dans le tétrachlorure de carbone.

ZUSAMMENFASSUNG

Es wurden die Bedingungen untersucht, unter denen Kupfer(I) durch Dithizon (H_2Dz) extrahiert werden kann. Die Zusammensetzung des orangebraunen primären Dithizonates ist Cu(HDz) mit $\lambda_{max} = 490$ nm, $\varepsilon_{max} = (28.0 \pm 0.2) \cdot 10^3$ in $CHCl_3$ und $\lambda_{max} = 480$ nm, $\varepsilon_{max} = (21.3 \pm 0.3) \cdot 10^3$ in CCl_4. Einige Reaktionen wurden untersucht.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF TRACES OF THALLIUM IN ZINC AND ZINC-BASE ALLOYS

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(Received 1st June 1971)

Thallium(III) is often determined colorimetrically[1] by means of the iodine liberated from iodide, while thallium(I) is determined by extraction as its dithizonate[2]. Gur'ev[3] was the first to report the extraction of an anionic chlorocomplex of thallium(III) with methyl violet and its spectrophotometric determination. This was followed by studies in which thallium(III) was extracted as the bromo/chloro complex along with methyl violet into benzene[4] or amyl acetate[5]. The use of other dyes such as brilliant green[5] and crystal violet[6-8] has also been reported.

Woolley[9] separated traces of thallium from cadmium and tin by extraction of its bromo complex into isopropyl ether and then completed the determination with rhodamine B. The British Standards Institution[10] applied this method for the determination of thallium in zinc and zinc-base alloys. The present work deals with a study of the optimal conditions for the extraction of thallium as an ion pair of its bromo complex and crystal violet into isopropyl ether and its application to the analysis of zinc and its alloys used in die casting.

EXPERIMENTAL

Reagents

Standard thallium solution: Dissolve 1.235 g of thallium sulphate (BDH AnalaR) and make up to 100 ml with 10% (v/v) nitric acid. Dilute this solution with water, as and when required, to give a working solution of 2.0 μg Tl ml^{-1}.

Methyl violet, crystal violet, malachite green, rhodamine B and thymol blue. Dissolve 0.2 g of each of the dye separately in 100 ml of water.

Bromine–bromide mixture. Mix 25 ml of bromine (E. Merck G.R.) well with 225 ml of hydrobromic acid (E. Merck G.R., *d* 1.46–1.49).

All other reagents used were of analytical grade.

Apparatus

Absorbance measurements were made with a matched pair of 1.000-cm corex cells on Beckman DU spectrophotometer, with a tungsten lamp as the light source.

Preliminary studies

Quantitative extraction of thallium as its bromo complex into isopropyl ether in a single equilibration has been reported[10]. Hence the optimal conditions for the reaction of the bromo complex in the organic phase with crystal violet were studied, by equilibrating the organic phase with an aqueous solution containing crystal violet and hydrobromic acid. The organic phase was transferred to a 25-ml volumetric flask and made up to the mark with the solvent. Its absorbance (*A*) was measured at 595 nm.

Effect of acidity. With 10 μg of thallium in a 0.002% solution of crystal violet, the variation of A_{595} as a function of hydrobromic acid concentration (0–1.0 *M*) was studied and is shown in Fig. 1 (curve I). Maximum absorbance was observed when the hydrobromic acid concentration in the aqueous phase was 0.1 *M* or less; 0.05 *M* acid was used in further experiments.

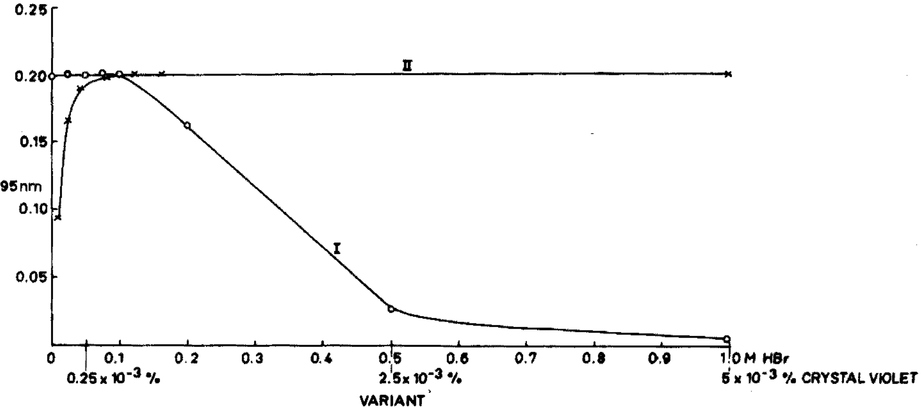

Fig. 1. Effect of HBr and crystal violet concentrations on the extraction of thallium. Tl 10 μg. Volume of organic phase 25 ml. Curve I: crystal violet 0.002%, c_{HBr} varied. Curve II: HBr 0.05 *M*, crystal violet varied.

Effect of reagent concentration. The variation of A_{595} as a function of crystal violet concentration (0.00005–0.005%) is also shown in Fig. 1 (curve II). Maximum absorbance was obtained when the dye concentration exceeded 0.0005%; a 0.002% dye concentration was employed in further experiments.

Sensitivity. When 0.05 *M* hydrobromic acid and 0.002% crystal violet were used, the amount of thallium was varied between 5 and 50 μg. A linear calibration curve was obtained with a molar absorptivity of $1.02 \cdot 10^5$ at 595 nm. Other basic dyes like methyl violet, thymol blue and malachite green were also studied in this particular solvent, the same quantities of thallium, hydrobromic acid and the dye being maintained. The absorbance of the extracted ion pair at the λ_{max} of the corresponding system was measured. The results are recorded in Table I along with similar results in other solvents from the literature. Rhodamine B and crystal violet in isopropyl ether provide the greatest sensitivity. These two dyes, when used with benzene or toluene as the solvent, are less sensitive. Crystal violet in isopropyl ether was used in further experiments.

Effect of various cations. The effect of other cations, such as Al^{3+}, Cu^{2+}, Mg^{2+}, Fe^{3+}, Pb^{2+} and In^{3+} associated with thallium(III) in zinc-base alloys used in the die casting, was studied by analysing synthetic mixtures containing 5 μg of thallium(III), 1.0 g of zinc(II) and different amounts of the other metal ions, under the same conditions as for the calibration curves. The results (Table II) showed that copper and lead

TABLE I

SENSITIVITY OF THE METHOD FOR THALLIUM WITH DIFFERENT DYES[a]
(Tl = 10 µg, HBr = 0.05 *M*, dye concentration = 0.002%, final volume of organic phase = 25 ml)

Dye	λ_{max} (nm)	$A_{\lambda_{max}}$ (1.0 *cm path length*)
Thymol blue	590	0.030
Crystal violet in toluene or benzene	605	0.103
Methyl violet	590	0.125
Malachite green	625	0.160
Rhodamine B in benzene	610	0.174
Crystal violet	595	0.201
Rhodamine B	610	0.215

[a] Unless otherwise stated the organic solvent is isopropyl ether.

TABLE II

EFFECT OF OTHER IONS ON THE DETERMINATION OF THALLIUM
(Tl = 5 µg, Zn = 1 g, crystal violet = 0.002%, acidity 0.05 *M* HBr, volume of organic phase = 25.0 ml)

Other ions added		*Tl found* (*µg*)	*Difference* (*µg*)
Ion	*Amount* (*mg*)		
—	—	13.0[a]	—
Al	50	12.80	−0.2
	100	13.10	+0.1
Cu	10	13.20	+0.2
	20	13.55	+0.55
Mg	0.5	12.65	−0.35
	1.0	12.95	−0.05
Fe	0.75	12.65	−0.35
	1.5	12.70	−0.30
Pb	0.03	13.10	+0.10
	0.06	13.70	+0.70
In	0.005	12.85	−0.15
	0.01	13.15	+0.15
Al Cu Mg Fe Pb In	50 10 0.5 0.7 0.03 0.005	12.95	−0.05
Al Cu Mg Fe Pb In	100 20 1.0 1.5 0.06 0.01	13.10[b] 12.95[b]	+0.10 −0.05

[a] Zinc sample contained 8 p.p.m. of Tl.
[b] After scrubbing the organic phase containing bromo complexes.

interfered when present in high amounts. This interference was easily eliminated by scrubbing the organic phase containing the bromo complex once or twice with 25 ml of 1.8 *M* hydrobromic acid containing 0.1 ml of bromine water (Table II). Since the separation of traces of thallium from tin and cadmium has already been reported[9], the behaviour of these two elements was not studied.

Application of the method

In the absence of a standard sample, the method was tested by the standard addition technique. Zinc sample Zn-1 was analysed with and without the addition of 5 and 10 μg of thallium(III) following the procedure given below. In another set, the thallium in the Zn-1 sample was extracted out and then analysed with and without the addition of 5 and 10 μg of Tl (Zn-2 sample). The results are given in Table III. The recovery of added thallium is quite satisfactory.

TABLE III

DETERMINATION OF TRACES OF THALLIUM IN ZINC

Sample taken (1 g)	*Tl added (μg)*	*Tl obtained (μg)*	*Total Tl content in the sample (μg)*
Zn-1	—	8.0	8.1
		8.2	
		8.1	
Zn-1	5.0	13.35	13.25
		13.15	
		13.25	
Zn-2	—	0.0	0.0
	5.0	5.0	5.0
	5.0	5.1	5.1
	10.0	10.0	10.1
Zn-3[a]		12.05	12.0±0.14
		11.85	
		12.10	
		12.15	
		11.90	
		11.85	

[a] This contained all the impurities shown for the last sample in Table II, as well as 10 mg Cd and 40 μg Sn.

Procedure

Weigh about 1 g of zinc (or alloy) sample, accurately to 1 mg, into a 100-ml beaker. Add 5 ml of bromine–bromide mixture and 5 ml of water and cover the beaker with a watch glass. Swirl the contents of the beaker intermittently. After the dissolution of the sample, place the beaker on a sand bath, and expel the excess of bromine without reducing the volume significantly. Cool the solution, transfer it into a 100-ml separating funnel and dilute to about 25 ml. Equilibrate this with 25 ml of isopropyl ether for 2 min. Allow the layers to separate well and discard the aqueous phase. Scrub the organic phase twice with 25 ml of 1.8 *M* hydrobromic acid containing 0.1 ml of bromine water. Discard the aqueous phase each time. Equilibrate the organic phase with 20 ml of a mixture containing 0.05 *M* hydrobromic acid and 0.002%

crystal violet for 2 min, allow the phases to separate, and discard the aqueous phase. Remove the water droplets in the stem of the separating funnel with filter paper. Transfer the organic phase to a 25-ml volumetric flask and make up to the mark with ether. Measure the absorbance of this extract at 595 nm against the corresponding reagent blank. Compute the thallium content from a calibration curve.

DISCUSSION

Many of the basic dyes mentioned in Table I give maximum colour with about 0.05 *M* hydrobromic acid in the aqueous phase (along with the dye). Hence the sensitivity of the methods with different dyes were studied at this acidity. It is apparent from Table I that rhodamine B and crystal violet are the most sensitive for thallium, when isopropyl ether is used for extraction. However, the phase separation is better with crystal violet than with rhodamine B. The calibration curve was linear up to 50 μg of thallium(III). For the extraction of the coloured ion pair, the hydrobromic acid and the dye solution should be mixed just before extraction.

The interference caused by the presence of copper and lead can easily be overcome by scrubbing the organic phase (containing the bromo complex) with hydrobromic acid and bromine water before the equilibration with the dye. The results in Table III show that thallium at the 5-p.p.m. level can be determined by the proposed method. On analysing a sample containing about 12 p.p.m. of thallium, the standard deviation was found to be 0.14 p.p.m. (6 determinations).

In view of the work of Woolley[9], it should be possible to determine thallium at the 5-p.p.m. level in cadmium and tin also.

The authors wish to thank Dr. M. Sankar Das for his keen interest in this work.

SUMMARY

A method is described for the determination of thallium at 5 p.p.m. level in zinc and zinc-base alloys. Thallium is extracted as an ion pair of its bromo complex and crystal violet into isopropyl ether and the absorbance is measured at 595 nm.

RÉSUMÉ

On décrit une méthode pour le dosage du thallium (5 p.p.m.) dans le zinc et dans des alliages à base de zinc. On procède à une extraction du bromocomplexe dans l'éther isopropylique. L'absorption est mesurée à 595 nm.

ZUSAMMENFASSUNG

Es wird eine Methode für die Bestimmung von Thallium in Zink und Zinklegierungen in der Grössenordnung 5 p.p.m. beschrieben. Thallium wird mit Isopropyläther als Bromokomplex-Kristallviolett-Ionenpaar extrahiert und die Extinktion bei 595 nm gemessen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A GAS CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF LOW CONCENTRATIONS OF THE CHLORIDE ION

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(Received 17th July 1971)

The determination of trace amounts of chloride has always been one of the major problems of analytical chemistry. Chloride cannot be amplified readily unlike bromide and iodide; the only amplification methods available are exchange reactions which have well-known deficiencies. The nephelometric methods were probably the most viable until the development of the mercury(II) thiocyanate reaction, but this has generally superseded earlier methods. Although it has been claimed recently that by the use of precision spectrophotometry, this method can be operated at the 15-p.p.b. level[1], the generally accepted lower limit is only about 1 p.p.m.

It occurred to us that if the chloride ion could be volatilized in some way, it would be possible to use sensitive gas-chromatographic methods for its determination. A possible means was conversion to volatile phenylmercury(II) chloride, for this and similar compounds can be readily determined by gas–liquid chromatography. Various organomercury(II) compounds have been determined in biological materials by conversion to the chloride with hydrochloric acid followed by extraction and injection on to a gas chromatographic column[2–5]; the limit of detection for methylmercury(II) chloride is 10^{-12} g when an electron capture detector is used.

With respect to chloride, the success of such a method would depend on the ease with which chloride in aqueous solution could be converted quantitatively to phenylmercury(II) chloride. It was found that on adding phenylmercury(II) nitrate to an acidified aqueous chloride solution, phenylmercury(II) chloride was rapidly formed and could be quantitatively extracted by chloroform without interference from the phenylmercury(II) nitrate. The chloroform solution could then be subjected to gas–liquid chromatography. An extremely sensitive determination of chloride then became possible.

EXPERIMENTAL

Reagents

Phenylmercury(II) nitrate. An aqueous 0.1% (w/v) solution was prepared by dissolving the appropriate weight of reagent in warm distilled water. From this, a 0.01% solution was prepared by dilution.

Phenylmercury(II) chloride. A 0.1% (w/v) solution in chloroform was prepared

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from the compound obtained as described below.

Chloride standard solution. A standard solution of chloride (0.1 mg ml^{-1}) was prepared from A.R. sodium chloride. Other solutions were obtained by dilution.

Redistilled chloroform and analytical-grade acids were used.

Preparation of phenylmercury(II) chloride

This was prepared by adding a slight excess of phenylmercury(II) nitrate solution to an aqueous sodium chloride solution at pH 1–2. Phenylmercury(II) chloride precipitated readily as a white amorphous compound which was collected by filtration and dried in the oven at 100°. The dried compound was purified by sublimation at 0.1 mm Hg in a sublimation apparatus immersed in a paraffin bath at 150°.

Elemental analysis gave: 23.2% C, 1.5% H, 11.3% Cl; C_6H_5HgCl requires 22.99% C, 1.6% H, 11.3% Cl.

Thermal analysis

This was carried out on a Perkin-Elmer TGS-1 thermobalance in an atmosphere of nitrogen with 2-mg samples at a temperature scan rate of 20° min^{-1}.

Gas chromatography

A Pye "Series 104" Gas Chromatograph fitted with a heated flame ionization detector was used. The column (glass column, length 3 feet, i.d. 4 mm) was filled with 60–85 mesh Universal B (Phase Separations Ltd) coated with 2.5% diethylene glycol adipate. The temperatures used for column, detector and injector were respectively 180°, 200° and 200°. Nitrogen was used as the carrier gas at a flow rate of 80 ml min^{-1}.

RESULTS AND DISCUSSION

Choice of reagent

Of the many organomercury(II) compounds, the phenyl derivatives were chosen because they are easy to obtain, easy to handle and less toxic than the alkyl derivatives. Methylmercury(II) chloride volatilizes at 100° and is very toxic. Phenylmercury(II) nitrate was selected as the reagent, because it behaves as a simple salt, being more soluble in water, in which it is completely ionized, than in organic solvents; it decomposes when heated. On the other hand, phenylmercury(II) chloride is a covalent compound, being more soluble in organic solvents than in water and subliming readily when heated. Table I shows the solubilities of both compounds in water and chloroform, at room temperatures.

TABLE I

APPROXIMATE SOLUBILITIES (μg ml^{-1}) IN WATER AND CHLOROFORM OF PHENYLMERCURY(II) NITRATE AND CHLORIDE (20°)

Compound	*Water*	*Chloroform*
Phenylmercury(II) nitrate	1,250	150
Phenylmercury(II) chloride	20	3,600

Exploratory investigations showed that on treating an aqueous solution of sodium chloride, made acid with 0.1 *M* nitric acid to pH 1–2, with an excess of an aqueous 0.1 % solution of phenylmercury(II) nitrate, an instantaneous precipitation of phenylmercury(II) chloride occurred. This precipitate is readily soluble in chloroform or benzene and can be extracted from the aqueous solution by these solvents. The formation of phenylmercury(II) chloride is not dependent on the presence of free hydrochloric acid, but occurs whenever a chloride solution is acidified to pH 1–2 and treated with phenylmercury(II) nitrate. The identity of the compound obtained in this way was confirmed by melting point, elemental and thermal analysis, and gas chromatography. The data corresponded with those obtained from an authentic sample of phenylmercury(II) chloride.

Thermal and gas chromatographic properties

The thermal analysis results indicated favourable prospects for the successful gas chromatography of phenylmercury(II) chloride; the compound has excellent volatility and thermal stability (Fig. 1), 100% volatilization occurring at about 268°.

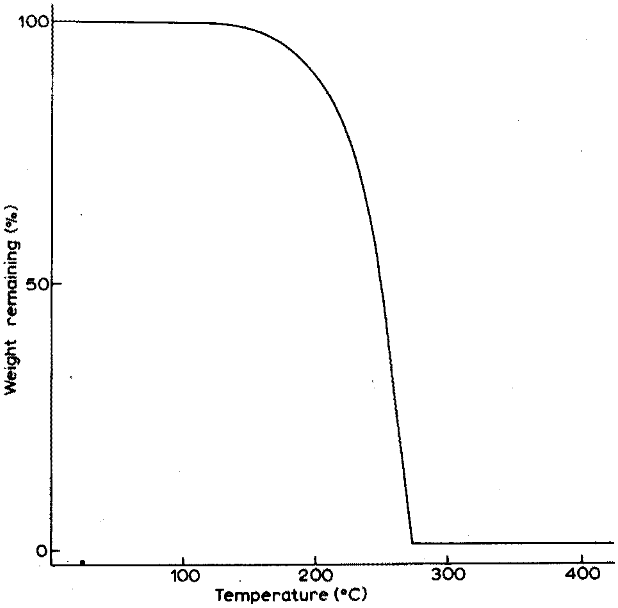

Fig. 1. Thermogram obtained for phenylmercury(II) chloride.

In order to find the most suitable stationary phase for gas chromatography of phenylmercury(II) chloride, the following liquid phases coating the same solid support (Universal B, 60–85 mesh) were tried: Apiezon L, Silicone Gum Rubber E301, Fluorosilicone Oil FS 1265, Fluorolube HG 1200 and diethylene glycol adipate at a loading level of 2.5%. Best results were achieved with the last one, and sharp, well-defined peaks, with little solvent tailing were obtained. Generally the more polar the liquid phase used, the better the results achieved. The columns were preconditioned for a period of about 36 h at the operating temperature. Glass columns were always used and the most suitable operational conditions were found to be: column temperature

180°, detector temperature 200°, injection port temperature 200° and carrier gas flow rate 80 ml min^{-1}, with a straight on-column injection. Figure 2 shows the chromatogram obtained under the above conditions for the injection of 1 µl of a 0.1% chloroform solution of phenylmercury(II) chloride.

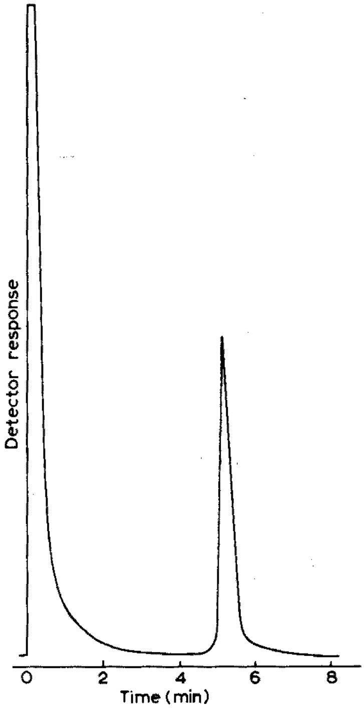

Fig. 2. Chromatogram of a 0.1% chloroform solution of phenylmercury(II) chloride, attenuation 2×10^2.

Once favourable conditions for the gas chromatography of phenylmercury(II) chloride had been obtained, the relationship of the chloride concentration to the detector response was studied. A standard solution (113.2 µg Cl ml^{-1}) of phenylmercury(II) chloride was prepared in chloroform and other solutions were made by dilution. Portions (1 µl) of these diluted solutions were injected on to the chromatographic column, under the given operational conditions, and the corresponding peaks were measured. However, before reproducible peaks could be achieved, it was necessary to make four injections, which indicated that there was some absorption on the stationary phase. This happened in all quantitative measurements, and was particularly noticeable when the column was brought into use after a period of idleness. An average of five injections for each solution was taken, and when both peak area and peak height were related to the concentration of chloride in the solution, straight lines were obtained, the best interval being obtained between 5.0 and 100.0 µg Cl ml^{-1} (Fig. 3). The limit of detection for the flame ionization detector under the optimal operational conditions (1 µl injection) was established as $20.3 \cdot 10^{-9}$ g of phenylmercury(II) chloride, which is equivalent to $2.3 \cdot 10^{-9}$ g of chloride.

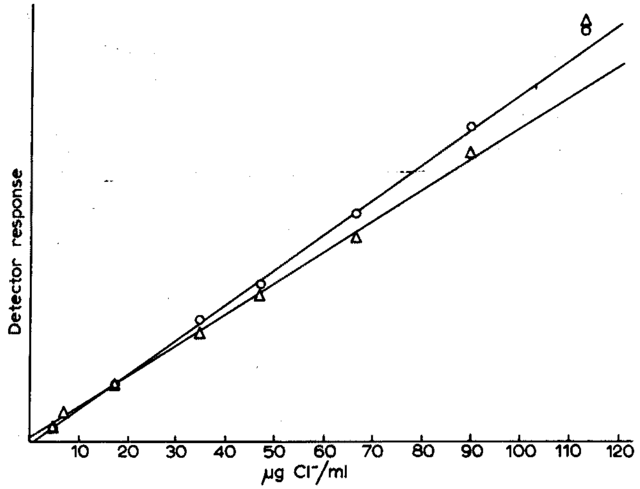

Fig. 3. Calibration graph for phenylmercury(II) chloride. (⊙) Peak height; (△) peak area.

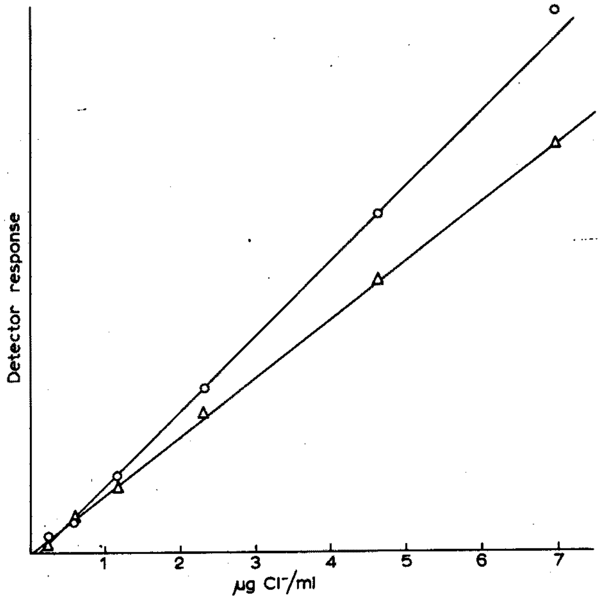

Fig. 4. Calibration graphs for phenylmercury(II) chloride. (⊙) Peak heights; (△) peaks areas. The points shown are the average results of 5 injections.

Development of analytical method

The primary purpose of this work was to determine very low concentrations of chloride; hence more dilute solutions of phenylmercury(II) chloride in chloroform and larger injected volumes were studied.

A standard solution of phenylmercury(II) chloride in chloroform with 11.32 µg Cl ml^{-1} was prepared and other solutions were obtained from this by dilution. These solutions (10 µl of each) were injected onto the column under the conditions recommended above, and calibration graphs were prepared (Fig. 4). The best interval of chloride concentration for quantitative purposes was found to be between 0.4 and 7.0 μg Cl ml^{-1} of the chloroform solution. Calibration graphs prepared this way were used for all subsequent determinations. These results indicated that the method offered exceptional possibilities for the determination of chloride at very low levels.

For the determination of chloride in aqueous solution, the initial procedure was as described below.

Standard aqueous sodium chloride solutions (2 ml), 1 ml of 0.1 *M* nitric acid and 3 ml of aqueous 0.1 % reagent solution were placed in a 50-ml separatory funnel and the volume of the aqueous phase was adjusted to 30 ml with water. The funnel was then shaken for 1 min. Phenylmercury(II) chloride was extracted with 7-ml and 3-ml portions of chloroform, the funnel being shaken for 1 min each time. The layers were allowed to separate and the extracts were collected in a 10-ml graduated flask, being diluted finally with chloroform to that volume if necessary. One microlitre of this solution was injected onto the chromatographic column.

These conditions were used to establish the effect of amount of reagent and pH as well as the nature of the acid used on the quantitative formation of phenylmercury(II) chloride. Interfering ions were also studied. It was found necessary to use 1 ml of an aqueous 0.01 % solution of the reagent for every 10 μg of chloride per millilitre of aqueous solution (10 p.p.m.), although a moderate excess of reagent did not cause any deleterious effect. Quantitative extraction was obtained in the pH range 0.0–4.5; percentage extraction decreased rapidly as the pH was further increased. A pH value of about 1.5 was selected. Nitric, sulphuric and perchloric acids were tried, of which perchloric acid was the most suitable.

The influence of other species on the reaction and the extraction process was studied; diverse ions were added to the solution before the formation of the organomercury(II) chloride. Of the common ions studied, only silver, mercury(I), mercury(II), bromide, iodide, thiocyanate, cyanide and nitrite interfered, and must not be present in the solution.

As the purpose of this work was to provide a method for the determination of very low concentrations of chloride, it might be necessary to handle large volumes of sample and to extract the phenylmercury(II) chloride with a small volume of solvent. This could then be concentrated to a very small volume. By injecting onto the chromatograph the greatest size of sample that the apparatus can admit, it should then be possible to detect very low concentrations of chloride. The following procedure was found to be successful.

Recommended procedure

To a 500-ml separatory funnel, transfer 250 ml of the sample, add 2 ml of perchloric acid (60 % w/w) or enough to obtain a final pH of about 1.5, and 1.5 ml of reagent (aqueous 0.01 % solution) for each 10 μg of chloride. Add 10 ml of chloroform. Shake the funnel vigorously for 1 min and allow the layers to separate. Collect the extract and repeat the extraction with 5 ml of chloroform, collecting the extract again. Concentrate the collected organic phase in a pear-shaped distillation flask until about 2 ml remains in the distillation flask, and then pour into a 5-ml graduated flask, washing the distillation flask twice with chloroform and completing the volume to the mark. Inject five 10 μl portions of this solution onto the chromatograph, measuring each separately, and take the average of the measurements.

To extract quantitatively the phenylmercury(II) chloride from such a large volume of aqueous solution, it was found that two extractions, with 10 ml of chloroform the first time and 5 ml the second, were sufficient. An increase in the volume used in both steps showed no improvement over the extraction procedure described.

When this procedure was applied to 250 ml of aqueous solution, the limit of detection was found to be 0.006 μg of chloride per millilitre in the original aqueous solution, *i.e.* 0.024 p.p.b.

Precision and accuracy

With this procedure three test runs with different concentrations of chloride were made to establish the precision and accuracy of the method. The data are given in Table II.

TABLE II

PRECISION AND ACCURACY DATA FOR THE GAS CHROMATOGRAPHIC DETERMINATION OF CHLORIDE

Cl taken (*μg ml*$^{-1}$)[a]	*No. of detns.*	*Mean Cl found* (*μg ml*$^{-1}$)[b]	*S*	S_r (%)	*Mean error*	*Rel. mean error* (%)
Peak height measurements						
0.008	7	0.010	0.0029	29.0	+0.002	25.0
0.020	10	0.019_4	0.0014	7.2	−0.0006	3.0
0.060	6	0.053_3	0.0024	4.5	−0.0007	11.6
Peak area measurements						
0.008	7	0.009_7	0.0031	31.9	+0.0017	21.3
0.020	10	0.019_1	0.0017	8.9	−0.0009	4.5
0.060	6	0.056	0.0018	3.2	−0.004	6.6

[a] These quantities are equivalent to a final concentration in the extract of 0.4, 1.0 and 3.0 μg Cl ml^{-1} respectively.

[b] Values obtained subtracting the blank.

Blank determinations consistently corresponded to about 0.002 p.p.m. of chloride in the aqueous sample, but this value would vary, depending on the source of the reagents used. Blank values were deducted from all the values quoted. The sensitivity of the method in this form and its reproducibility at the lowest level are remarkable.

CONCLUSIONS

The investigations done so far with a flame ionization detector indicate the utility of the proposed system for the determination of traces of chloride. The use of an electron capture detector should improve markedly the limit of detection; this factor together with modifications in the volumes of aqueous solution and organic extractant used, as well as the injection of the greater sample sizes possible with the electron capture method, should permit the determination of chloride far below the present levels.

A further project is the separation and simultaneous determination of the three halides. This should be possible, for preliminary tests indicate that phenylmercury(II) bromide and iodide behave similarly to the chloride compound.

The work described here forms part of more extended studies of these phenylmercury halides in which the development of spectrophotometric and atomic absorption methods with the same scope are included.

One of us (J.A.R.) is grateful to the University of Santiago de Compostela for leave of absence, and to the Consejo Superior de Investigaciones Cientificas and the Ministerio de Educacion y Ciencia of Spain for financial support.

SUMMARY

A new method for the determination of low levels of chloride is proposed. Chloride in aqueous solution is readily converted to phenylmercury(II) chloride by treatment with phenylmercury(II) nitrate at *ca.* pH 1.5 and the covalently bound chloride is quantitatively extracted into chloroform. This solution is concentrated by distillation and analysed by gas chromatography. The method is suitable for 0.4–7.0 μg Cl ml^{-1} of the chloroform extract. As little as 0.008 p.p.m. of chloride in aqueous solutions can be determined when a flame ionization detector is used.

RÉSUMÉ

On propose une nouvelle méthode pour le dosage des chlorures en faibles quantités. Elle est basée sur la formation de chlorure de phénylmercure(II) par traitement avec le nitrate de phénylmercure(II) à un pH d'environ 1.5; la liaison covalente du chlorure est alors extraite quantitativement dans le chloroforme. La solution obtenue est concentrée par distillation et analysée par chromatographie gazeuse. Cette méthode convient pour des concentrations de 0.4 à 7.0 μg Cl ml^{-1} de l'extrait chloroforme. On peut doser jusque'à 0.008 p.p.m. de chlorure en solution aqueuse, si l'on utilise un détecteur d'ionisation à flamme.

ZUSAMMENFASSUNG

Es wird eine neue Methode für die Bestimmung kleiner Chloridgehalte vorgeschlagen. Chlorid in wässriger Lösung wird durch Behandlung mit Phenylquecksilber(II)-nitrat bei *ca.* pH 1.5 leicht zu Phenylquecksilber(II)-chlorid umgewandelt und das kovalent gebundene Chlorid quantitativ mit Chloroform extrahiert. Diese Lösung wird durch Destillation konzentriert und durch Gaschromatographie analysiert. Die Methode eignet sich für 0.4–7.0 μg Cl ml^{-1} im Chloroformextrakt. Bei Verwendung eines Flammenionisationsdetektors können so geringe Gehalte wie 0.008 p.p.m. Chlorid in wässrigen Lösungen bestimmt werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SULPHUR DIOXIDE AS A STANDARD FOR THE DETERMINATION OF SULPHUR BY COMBUSTION

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(Received 15th May 1971)

Earlier work has shown that the Sulmhograph sulphur analyser is a suitable instrument for the precise determination of low concentrations (1–100 p.p.m.) of sulphur in tin[1]. The preliminary work was carried out with a sulphur-containing organic compound (sulphanilic acid) and sulphur dioxide gas for standardization purposes. For the analysis of tin it is necessary to weigh out very small amounts of sulphanilic acid (about 150 μg). The difficulties of weighing this small quantity were considered to be too great for a routine method. Sulphur dioxide can be diluted to the required levels by means of suitable gas dilution systems and this has more likelihood of becoming a universal standard. The use of sulphur dioxide is not so much choice as necessity, since at present there seems to be no other suitable standard such as those available to the steel industry.

For the analysis, the sample is burned in oxygen, and it is reasonable to suppose that some sulphur trioxide is formed. Sulphur dioxide is relatively easy to adsorb but the trioxide is more difficult[2] requiring such devices as impingers to collect the acid mist[3]. It was therefore thought unlikely that much sulphur trioxide would be collected in the short path length of the Sulmhograph cell. For accurate work it was considered that the sulphur oxides from the standard material must be generated at the same point in the furnace tube as were those from the sample in order that the same SO_2/SO_3 ratio be maintained. It was expected that standardization would involve only the injection of the required quantity of sulphur dioxide obtained by dilution of the pure gas. The eventual realization that the cell was not quantitative with respect to sulphur dioxide indicated that the standardization was a more complex problem.

It has been established that the Sulmhograph gives precise results and, by comparison to colorimetric analysis (methylene blue), was assumed to be accurate. The colorimetric method is reliable enough to detect gross errors in standardization but not precise enough to identify more subtle ones. Since sulphur dioxide had been chosen as the standard some work was therefore directed to comparisons between this and other standard materials, such as sulphanilic acid and tin(II) sulphide. These comparisons gave the clue to the technique of standardization and led to the comprehensive system described herein, which in turn led to a fuller assessment of the standardizing system. The assessment involved the analysis of a number of materials chosen to give a range of sulphur contents (p.p.m. to %), different combustion times (very rapid to several minutes) and to include different environments of the sulphur atom (inorganic/organic, sulphide/sulphate). The sulphur content of each material was either known (pure compound) or was checked by another method and, to avoid any prejudice, by other analysts.

Clearly some aspects of the work were developed interdependently and it would be extremely confusing to attempt a description in chronological order. An integral part of this development was a study of the analysis of tin and, for the sake of clarity, this is reported separately. The remaining experimental work is subdivided into two parts: (*a*) that leading to the design of the standardization system and (*b*) its assessment.

EXPERIMENTAL

Apparatus

Instrument. Wösthoff Sulmhograph 12, sulphur analyser. Wösthoff electrostatic precipitator. Carbolite 4 tube furnace, type CFM4/1450/VT4. Alumina furnace tubes (500 mm × 20 mm i.d.). Unglazed porcelain boats (50 mm × 10 mm × 10 mm).

Standardisation equipment. Wösthoff gas forwarding pump, type M22aX. Wösthoff gas dosing devices, types DS10 and DS2. Mixing vessels, borosilicate glass.

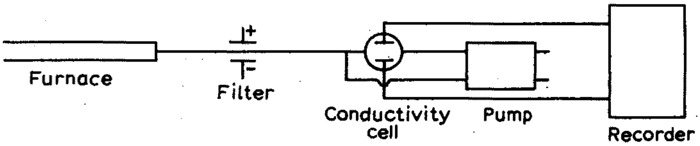

Fig. 1. Sulmhograph sulphur analyser (schematic).

The Sulmhograph (Fig. 1) consists essentially of a combustion tube, an electrostatic filter[1], an absorption cell and a precision pump. The development and principles of the instrument have been described[4-7]. The two-piston pump is switched so that one or both pistons are effective in drawing the gas stream through the furnace. The gas flow can be either 326 ml min^{-1} or 652 ml min^{-1}, but in either case only 326 ml min^{-1} passes through the cell which therefore has two levels of sensitivity. In general a gas flow of 652 ml min^{-1} is preferred to reduce the effects of adsorption in the fur-

TABLE I

MEASURING RANGES OF SULMHOGRAPH USED

	Gas flow (ml min^{-1})	*Full scale deflection*
Cell I	326	20 µg
0.0004 *N* H_2SO_4		100
0.004 *M* H_2O_2	652	40
		200
Cell II	326	1 mg
0.02 *N* H_2SO_4		5
0.02 *M* H_2O_2	652	2
		10

nace tube. Also there are two levels of sensitivity available at the recorder of ratio 5:1. Since the instruments are manufactured to customer specification, two cells were obtained to cover a wide range of analyses (Table I).

The gas forwarding pump has three pistons which can deliver gas at different rates: piston 1, 50–500 ml min^{-1} in steps of 50 ml min^{-1}; piston 2, 50–500 ml min^{-1} in steps of 50 ml min^{-1}; and piston 3, 100 ml min^{-1} fixed. The pump was calibrated against a 1-l burette by means of the soap bubble technique; the burette was itself calibrated against water by weight.

The dosing devices. Dosing device DS2 is a rotating dosing cock of Teflon-graphite. The interchangeable cocks have nominal bores of 1, 1¾, 2, 2½, and 3 mm corresponding to approximately 0.02, 0.04, 0.05, 0.07 and 0.1 ml respectively. For calibration, a given number of doses of sulphur dioxide was absorbed in 3% w/v hydrogen peroxide (number 2 sinter glass bubbler, carrier gas 50 ml min^{-1}) and the resulting sulphuric acid was determined with standard sodium hydroxide delivered from Jencons piston burettes. For optimal accuracy it is desirable to recalibrate the dosing cocks with each cylinder of sulphur dioxide. In this way changes in purity are compensated for as changes in apparent volume.

Dosing device DS10 utilises a glass "U" tube which is alternately filled with sulphur dioxide and flushed with oxygen. It is used and standardized in the same way as dosing device DS2. The "U" tubes have nominal volumes of 0.4, 1 and 2 ml.

The standardization system is based on injecting known quantities of sulphur dioxide into a known oxygen stream. The process of injection is illustrated in Fig. 2. As the dosing cock rotates, it is alternately filled with sulphur dioxide and flushed with oxygen. In the closed position the gas streams pass at about atmospheric pressure through the bypass circuits.

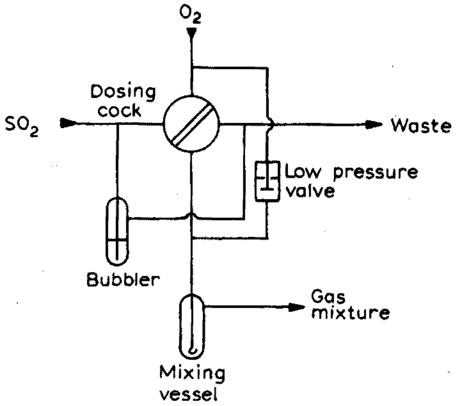

Fig. 2. Dosing device.

The complete circuits are shown in Fig. 3. All the tubing is PTFE joined to glassware and dosing devices by Viton couplings. In the dilution stage (Fig. 3a) the sulphur dioxide is injected into the oxygen stream supplied by the forwarding pump. The rate of oxygen flow is altered by the pump gears and, together with the selection of dosing cocks and variable dosage (1 to 10 doses/min), a wide range of dilutions is possible. A similar arrangement is used for the injection into the furnace tube. If it is

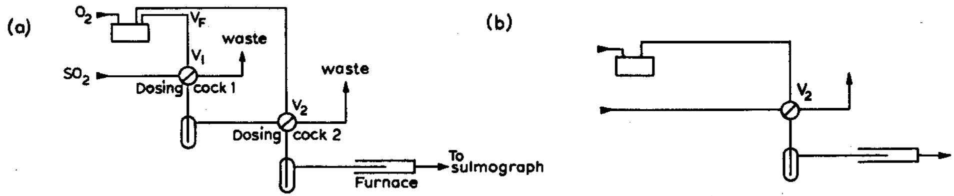

Fig. 3. Dilution and injection of sulphur dioxide (schematic). (a) Injection of diluted gas. (b) Injection of undiluted gas.

required to inject doses of pure sulphur dioxide the dilution stage is not used (Fig. 3b).

The weight of sulphur delivered by dosing device 2 alone (Fig. 3b)

$$= \frac{32.07 \times 273 \times V_2N_2P}{21.89 \times 760 \times T} = \frac{0.5263\ V_2N_2P}{T}\ \text{mg}$$

The weight of sulphur delivered by both devices (Fig. 3a)
= weight from 2 × dilution at 1

$$= \frac{526.3\ V_1n_1V_2N_2P}{V_FT}\ \mu\text{g}$$

where V_1 = volume of 1 (ml), n_1 = number of doses/min of 1, V_2 = volume of 2 (ml), N_2 = number of doses of 2, V_F = volume delivered by forwarding pump (ml min^{-1}), P = atmospheric pressure, T = atmospheric temperature.

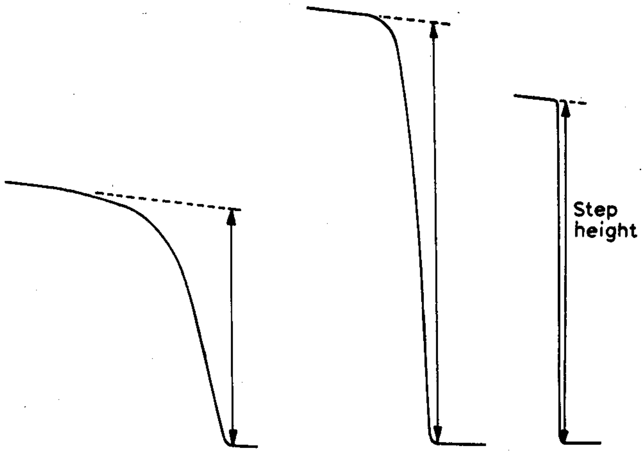

Fig. 4. Examples of combustion steps.

The shape of the combustion step (Fig. 4) is matched by selection of the rate of injection (slope) and the appropriate mixing vessel (slope and curvature), the latter chosen from the range 30, 75, 150, 300, 500 and 1000 ml. The rate of injection may be 1–10 doses/min or, by manual operation, continuously (about 14 doses/min).

The Sulmhograph is highly damped to ensure optimal precision and thus has a response too sluggish for the study of rapidly burning materials. The measuring

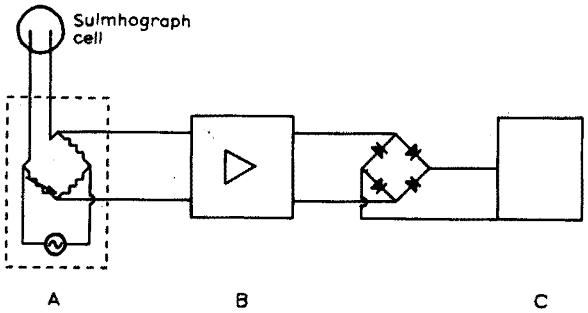

Fig. 5. Modification to Sulmhograph. (A) Wayne–Kerr universal bridge Type B 221. (B) General Radio Co. tuned amplifier Type 1232-A. (C) Bryans chart recorder Model 27000.

circuit was adapted (Fig. 5) to improve the response time but at the expense of precision. The original cell of the Sulmhograph was used and this still imposed a limitation in the response time as the sulphur dioxide was absorbed in one part of the cell and measured in another, the electrolyte being continuously circulated. The adaptation was therefore satisfactory for materials burning moderately quickly (about 1 sec to 1 min) but not for very rapid combustions (*e.g.* organic compounds). For combustion of more than about 1 min the Sulmhograph was used unmodified. All analyses reported here were performed with the unmodified instrument.

Development of standardization system

Investigations were carried out on the effects of tin, the absorption and dilution of sulphur dioxide and the use of different standards for the determination of sulphur in tin. Initially these effects were assumed to be unrelated but it became apparent that they were all different aspects of the same problem, namely standardization.

Effect of tin(IV) oxide. During the combustion of the tin specimens a quantity of tin(IV) oxide is carried over in the oxygen stream as a fine dust. It was expected that some of the sulphur dioxide would be adsorbed on this dust and become trapped in the electrostatic precipitator. In order to test the effect, tin(II) sulphide (5 mg) was analysed and the results were compared to those obtained for sulphide encapsulated in tin (1 g). For milligram amounts there was a significant difference between the free sulphide ($\bar{x}=22.6\%$, $s=0.6$) and the encapsulated sulphide ($\bar{x}=21.4\%$, $s=0.7$). Repeating the experiment with microgram quantities of tin(II) sulphide (800 μg) showed similar discrepancies. To ensure against any failure in the standardization, both sulphur dioxide and sulphanilic acid standards were employed. Typical results obtained are shown in Table II.

The results in column 1 were calculated with sulphur dioxide as standard while those in column 2 were referred to sulphanilic acid. Within the limits of precision, the salient feature is that the results for tin(II) sulphide (sulphanilic acid standard) and tin capsules (sulphur dioxide standard) agree with that obtained by the chemical method; the others do not. The following observations were also made: (*a*) the burning times of tin(II) sulphide and sulphanilic acid are similar (instantaneous); (*b*) the burning time of the tin capsules (20 sec) is similar to the time of injection of the sulphur dioxide.

The hypothesis was formed that for accurate analysis the sulphur dioxide

TABLE II

EFFECT OF TIN ON THE ANALYSIS OF TIN(II) SULPHIDE[a]

Sample	*SO_2 standard*		*Sulphanilic acid standard*	
	$\bar{x}$ (%)	*s*	$\bar{x}$ (%)	*s*
Sulphanilic acid	20.1	0.3	—	—
Capsules	20.6	0.5	19.1	0.7
Free sulphide	22.2	1.0	20.3	0.9

[a] The result obtained by chemical analysis was 20.3%.

evolved from the sample must be closely matched, not only by the amount but also by the rate of injection of the standard gas into the furnace tube. If this is correct the apparent discrepancy between encapsulated and free tin(II) sulphide obtained earlier with milligram quantities is explained as an error in standardization; this was subsequently shown to be correct.

Adsorption of sulphur dioxide. The instrument, and more particularly the standardization equipment, contains a number of pieces of glassware and many lengths of PTFE tubing. Although the adsorption of sulphur dioxide was likely to be small[8] it was considered necessary to test the effect on the different parts of the apparatus and in fact it was confirmed to be insignificant. However, the test did show that the Sulmhograph absorbs sulphur dioxide more efficiently at high partial pressure than it does at low partial pressure, indicating that the partial pressure of the standard gas must equal that of the sample and, more specifically, that changes in partial pressure must be matched by the standard gas.

Comparison of standards. The previous work[1] was carried out on different instruments in different places, facilities not being available to compare directly the two standard materials, sulphanilic acid and sulphur dioxide. The former was now analysed with the instrument standardized against the latter. There was some difference between the theoretical figure (18.5%) and the analytical figures (sample weight 150–200 μg, $\bar{x}=19.0\%$, $s=0.4$) obtained in this experiment; furthermore the analytical figure did not agree with that obtained earlier (see Table II, sample weight 700–900 μg, $\bar{x}=20.1\%$, $s=0.3$).

For standardization, diluted sulphur dioxide was injected into the instrument

TABLE III

ANALYSIS OF SULPHANILIC ACID; COLLECTED RESULTS

SO_2 standard		*Sample*			
No. of doses	≡ *wt. of S (μg)*	*Wt. of sample (μg)*	≡ *wt. of S (μg)*	*% S*	
				$\bar{x}$	*s*
10	22	150	30	19.0	0.4
10	115	100–900	20–180	18.9	0.4
25	120	700–900	140–180	20.1	0.3

in a number of discrete doses, the number depending on the weight of sulphur required. There was therefore a possibility that either the weight of sample or the number of doses or both contributed to these discrepancies. The effect of varying sample weight gave inconclusive results.

However, presenting all the results together (Table III) makes it clear that for a given number of doses *i.e.* 10, variation in sample weight had no noticeable effect on analysis. On the other hand, increasing the number of doses to 25 results in a significant variation in the analysis. This would imply that in this case the introduction of the standard into the furnace must match the instantaneous combustion of the sample.

Dilution of sulphur dioxide. It followed that some measure of the effect of dilution of the sulphur dioxide on its absorption in the cell was desirable. Different reaction rates (*i.e.* dilutions) were simulated by coupling a dosing device directly to the Sulmhograph via various mixing vessels and injecting one dose. The optimal precision was reached at about 75 ml and there was little to be gained by introducing a volume greater than 150 ml; further dilution only increased the analysis time. By good fortune the half volume of the furnace tube (the volume into which the sample released its sulphur dioxide) was about 75 ml. The results for cell II confirmed that there was no detectable permanent absorption on the glass and showed that the required degree of matching between standard and sample became less as the dilution increased. A slight fall-off at higher dilutions for cell I is thought to indicate a loss of absorbing efficiency and implies that a higher degree of matching is required for this cell.

Assessment of standardization system

Mild steel. The maximum weight of steel which could be contained in a covered porcelain boat during the violent combustion was about 0.6 g; pellets of about 0.4 g were therefore used. These were conveniently burned at a furnace temperature of 1350°, with a tin pellet (0.5–0.6 g, $\bar{x} = 4.9$ p.p.m.) as igniter. The tin was premelted in the cooler part of the furnace before combustion and the steel analysis was calculated after subtraction of the tin figure. The results ($\bar{x} = 314.2$ p.p.m., $s = 5.8$) were similar to those obtained with a Hilger and Watts automatic carbon and sulphur analyser ($\bar{x} = 312$ p.p.m.) standardised against a standard steel.

Dilution of SO_2: nil.

Injection*: $V_2 = 0.1$ ml, $N_2 = 1$ dose, injection rate = 100 ml min^{-1}.

Tin(II) sulphide. 5–6 mg was burnt in an open platinum crucible. The results ($\bar{x} = 20.4\%$, $s = 0.3$) were similar to those obtained by chemical analysis ($\bar{x} = 20.3\%$).

Dilution of SO_2: nil.

Injection: $V_2 = 1$ ml, $N_2 = 1$ dose, mixing vessel = none, injection rate = 100 ml/min^{-1}.

Barium sulphate (X-ray examination grade). The rate of decomposition of barium sulphate at elevated temperatures is very slow but can be increased by the addition of silica[9]. It can be further increased by the addition of potassium carbonate to form a melt. A convenient melt was given by 0.05 g $BaSO_4$, 0.1 g SiO_2 and 0.07 g K_2CO_3. At 1350° the results were $\bar{x} = 13.2\%$, $s = 0.1$, and at 1450°, $\bar{x} = 13.4\%$, $s = 0.1$

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* For explanation of V_2, N_2 etc. see Fig. 3.

(theoretical 13.7%). It would appear that sulphur dioxide has a detectable solubility in this melt.

Dilution of SO_2: nil.
Injection (1350°): $V_2 = 0.4$ ml, $N_2 = 13$ doses at 5/min, mixing vessel $= 75$ ml, injection rate $= 100$ ml min^{-1}.
Injection (1450°): $V_2 = 0.4$ ml, $N_2 = 13$ doses at 9/min, mixing vessel $= 75$ ml, injection rate $= 100$ ml min^{-1}.

Organic compounds. The organic compounds selected for examination were sulphanilic acid (analytical reagent grade), sulphamic acid (microanalytical reagent grade), and dibenzyl disulphide (microanalytical reagent grade).

The analysis of the organic compounds proved to be less straightforward than expected. For 5-mg samples (open platinum crucible, furnace temperature 1350°), the compounds gave different combustion steps (Fig. 6), a spiked step (a) being characteristic of sulphamic acid and dibenzyl disulphide, whilst a smooth step (b) was given by sulphanilic acid. These two shapes of step could be reproduced by injecting one dose of undiluted sulphur dioxide directly into the furnace tube (step a) and, by inserting a 30-ml mixing vessel between the dosing device and the furnace (step b). With an injection gas flow of 100 ml min^{-1}, this latter system gave just sufficient dilution to reproduce the smooth step. It seemed that the rate of release of sulphur dioxide by sulphamic acid and dibenzyl disulphide was faster than that by sulphanilic acid. Since it was unsatisfactory that different standards should be required for these materials, the speeds of combustion were reduced. This was

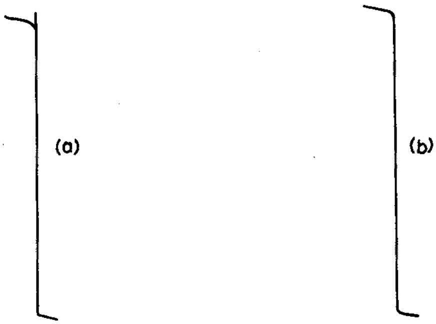

Fig. 6. Combustion of organic compounds at 1350°. (a) Step given by sulphamic acid and dibenzyl disulphide. (b) Step given by sulphanilic acid.

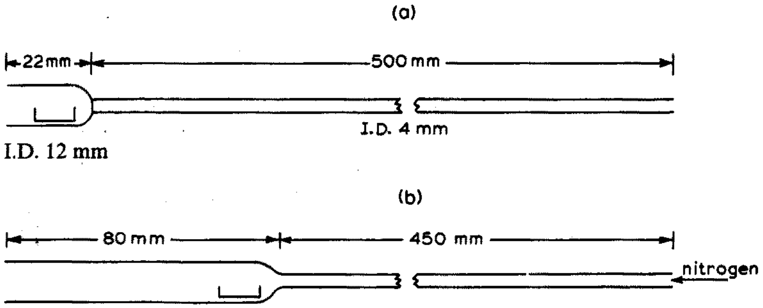

Fig. 7. Silica probes for analysis of organic compounds and oil. (a) Holder for organic compounds. (b) Holder for oil samples. In both cases, the platinum boat was 12 mm long, 8 mm wide and 4 mm high.

achieved by successively (*i*) reducing the temperature to 1200°, (*ii*) using a platinum boat mounted inside a silica probe (Fig. 7a) and, (*iii*) reducing the gas flow through the furnace to 326 ml min^{-1}. When all these changes were complete one standard gave satisfactory analyses for all three compounds (Table IV). The final arrangement was similar to that described by Pell *et al.*[6].

TABLE IV

ANALYSIS OF ORGANIC STANDARD COMPOUNDS
(Theoretical analyses: sulphanilic acid, 18.5%; sulphamic acid, 33.0%; dibenzyl disulphide, 26.0%)

Compound	*Sample wt. (mg)*	*Temp (°)*	*Sample holder*	*Furnace gas (ml min^{-1})*	*Standard*	*Mixing vessel*	*S*	
							$\bar{x}$ (%)	*s*
Sulphanilic acid	5	1350	Pt crucible	652	1 dose, 1 ml	30 ml	18.7	0.1
Sulphamic acid	5	1350	Pt crucible	652	1 dose, 1 ml	—	32.4	0.3
Dibenzyl disulphide	5	1350	Pt crucible	652	1 dose, 1 ml	—	25.7	0.3
Sulphanilic acid	5	1200	Pt crucible	652	1 dose, 1 ml	30 ml	18.4	0.1
Sulphamic acid	5	1200	Pt crucible	652	1 dose, 1 ml	—	31.4	0.3
Dibenzyl disulphide	5	1200	Pt crucible	652	1 dose, 1 ml	—	27.6	0.3
Sulphanilic acid	5	1200	SiO_2 probe	652	1 dose, 1 ml	—	18.7	0.1
Sulphamic acid	5	1200	SiO_2 probe	652	1 dose, 1 ml	—	33.2	0.1
Dibenzyl disulphide	5	1200	SiO_2 probe	652	1 dose, 1 ml	—	27.6	0.1
Sulphanilic acid	2	1200	SiO_2 probe	326	1 dose, 0.4 ml	30 ml	18.4	0.1
Sulphamic acid	2	1200	SiO_2 probe	326	1 dose, 0.4 ml	30 ml	33.2	0.2
Dibenzyl disulphide	2	1200	SiO_2 probe	326	1 dose, 0.4 ml	30 ml	26.2	0.1

Oil. The first few experiments indicated that the weight of the sample should be small and that the processes of volatilization and combustion should be separate. Oil (0.1 g) was weighed into a platinum boat mounted inside a silica probe (Fig. 7b). The probe was positioned in the furnace to give a reasonable rate of volatilization and the flow of nitrogen (100 ml min^{-1}) carried the vapour into the combustion zone (1350°, total gas flow 326 ml min^{-1}). The rear half of the furnace tube was packed with alumina beads to give a large surface area on which to trap and oxidize any free carbon. The particular oil was chosen because it volatilized as a single fraction. Again, the results ($\bar{x}=0.77$ %, $s=0.02$) compared favourably with those obtained with the Hilger and Watts analyser ($\bar{x}=0.75$%).

Dilution of SO_2: $V_1 = 2$ ml, $n_1 = 10$ doses/min, $V_F = 150$ ml min^{-1}
Injection: $V_2 = 0.07$ ml, $N_2 = 60$ doses at 10/min, mixing vessel = 150 ml, injection rate = 100 ml min^{-1}.

DISCUSSION

During analysis the sample is burned or decomposed at high temperature, mainly to sulphur dioxide. As the gases cool some sulphur trioxide is formed and this mixture passes into the absorption cell. The relevant reactions for these processes are represented by the equations:

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3 \tag{1}$$

$$SO_{2(\text{gas})} + H_2O_2 = H_2SO_{4(\text{cell soln.})} \tag{2}$$

$$SO_{3(\text{gas})} + H_2O = H_2SO_{4(\text{cell soln.})} \tag{3}$$

Equilibrium (1) is dependent on both temperature and partial pressure, the former probably being more important since it also controls reaction rate. Thus although low temperature favours the formation of sulphur trioxide, the rapid cooling ensures that a large proportion of sulphur dioxide remains. If reactions (2) and (3) were quantitative then the cell could be standardized by introducing a standard amount of sulphuric acid by any convenient means, *e.g.* standard acid directly into the cell or by burning a known amount of sulphur. If only one of the reactions is quantitative then the standard gas must follow the same route as the sample so that it undergoes the same temperature variations and establishes the same SO_2/SO_3 ratio.

For this instrument neither reaction is quantitative and in fact reaction (3) is better written as

$$SO_{3(\text{gas})} + H_2O = xH_2SO_{4(\text{cell soln.})} + (1-x)\,H_2SO_{4(\text{acid mist})} \tag{4}$$

because it is almost certain that most of the trioxide escapes absorption. The efficiency of each of these reactions depends on partial pressure and, since this varies as the combustion proceeds, it therefore follows that the standard must not only take the same route as the sample, but must also match the variations in partial pressure.

This, then, is the principle which has been adopted for the standardization of the Sulmhograph. The instrument is used to monitor the sample and by matching the combustion step with the standard, precise results can be obtained. The technique is satisfactory for a range of samples of differing sulphur contents producing widely differing partial pressures of sulphur dioxide; the only serious difficulty occurred with the organic standards (very high partial pressures). The only sample studied which did not agree with the theoretical value was barium sulphate and the discrepancy can be explained as a function of the solubility of sulphur dioxide in the melt.

No effort has been made to make the conversion to sulphuric acid quantitative and it is reasonable to suppose that the same principle will apply to other systems monitoring dilute gas streams (*e.g.* pollution control) and to other analyses (*e.g.* carbon). Clearly the accuracy with which an analysis can be carried out depends on the precision with which the combustion curve can be matched and the accuracy of calibration of the various dosing devices and pump speeds. During calibration a relative standard deviation of 0.002 was sought and obtained in every case except at the smallest dosing cock (0.0028). The dosing cocks were calibrated by absorbing a given number of doses in hydrogen peroxide and titrating with standard alkali, the latter being referred to MAR sulphamic acid. In all cases potentiometric end-points were taken (glass/calomel electrodes). The forwarding pump was referred to the weight of water delivered by a burette.

The successful analysis of the various materials suggests that this approach is correct. It has been shown that if a combustion can be matched by the standardisation system then a satisfactory analysis will result.

The author wishes to thank Mr. N. A. Murphy for much helpful discussion, Mr. A. Tune, for designing the modifications to the Sulmhograph, the Central Analytical Laboratory, Pilkington Brothers, Limited, St. Helens, Lancashire for co-operation in carrying out the collaborative analyses and the Directors of Pilkington Brothers, Limited and Dr. D. S. Oliver, Director of Group Research and Development, for permission to publish this article.

SUMMARY

A comprehensive system is described which enables sulphur dioxide to be used as standard in the determination of sulphur by combustion at microgram and milligram levels. The sulphur dioxide is injected into the furnace tube by a combination of gas dosing devices. The design and method of usage of the system are outlined. For accurate analysis the sulphur dioxide must be injected not only in the same quantity but also at the same rate as that released from the decomposing sample. The assessment of the system, by analysis of various different samples, confirms this conclusion.

RÉSUMÉ

On décrit un dispositif permettant d'utiliser l'anhydride sulfureux comme étalon, lors du dosage du soufre par combustion (à l'échelle micro- et milligramme). Le gaz sulfureux est injecté dans le tube du four par un système doseur, non seulement en même quantité, mais aussi à la vitesse correspondant à la décomposition de l'échantillon brûlé.

ZUSAMMENFASSUNG

Es wird ein System beschrieben, mit dem Schwefeldioxid als Standard bei der verbrennungsanalytischen Bestimmung von Schwefel im Mikrogramm- und Milligrammbereich verwendet werden kann. Das Schwefeldioxid wird dem Verbrennungsrohr durch eine Kombination von Gasdosiervorrichtungen zugeführt. Der Aufbau und die Anwendungsweise des Systems werden erläutert. Für die genaue Analyse muss das Schwefeldioxid nicht nur in der gleichen Menge, sondern auch mit der gleichen Geschwindigkeit zugeführt werden wie das Schwefeldioxid, das aus der sich zersetzenden Probe entsteht. Diese Folgerung wird durch die Analyse verschiedenartiger Proben bestätigt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SEPARATION OF MICROGRAM QUANTITIES OF DICARBOXYLIC ACIDS BY ANION-EXCHANGE CHROMATOGRAPHY

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(Received 15th June 1971)

In separations of dicarboxylic and tricarboxylic acids by means of anion-exchange chromatography several important acids give serious tailing[1,2] when applied in amounts comparable to those used in separations of monocarboxylic acids. As shown previously, the tailing which occurs in phosphate media cannot be ascribed to bad column efficiency. The most likely explanation is therefore that the ion-exchange isotherms of the tailing species are non-linear within the applied concentration range.

The main purpose of the present work is to elucidate the influence of the column loading upon the chromatographic separations and to eliminate the tailing by working with very small amounts of sample so that the ion-exchange isotherms are linear. These small amounts could not be detected by the automatic analysis methods applied previously, and for this reason a modified analysing system had to be developed.

EXPERIMENTAL

The analysis system described previously[3] is based upon chromic acid oxidation and subsequent colorimetric determination of chromium(III) ions at 600 nm. This system is used satisfactorily in the automatic determination of about 1 mg of separated carboxylic acids. Several of the acids studied in the present work gave serious tailing when milligram quantities were applied to the column, and for this reason the analysis method was modified to make it possible to decrease the amounts of added acids.

A differential amplifier was inserted after the photometer (LKB Multichannel Absorptiometer Type 5901A) to amplify the voltage difference resulting from the change in light intensity when a peak emerged. Attenuators on the front panel of the photometer were adjusted so that equal output signals were received from the measuring and reference photocells when the eluent mixed with reagent solution was passed through the photometer. The amplification was increased by a factor of five (about 0.01 absorbance units full scale) compared to that used previously.

When this amplification was applied, serious disturbances were observed which could be related to a leakage of polyglycol from the heating bath into the teflon reaction coil. When this coil was replaced by a glass coil the noise level was found to be reasonable but the method was not sensitive enough for an analysis of complicated mixtures of seriously tailing acids.

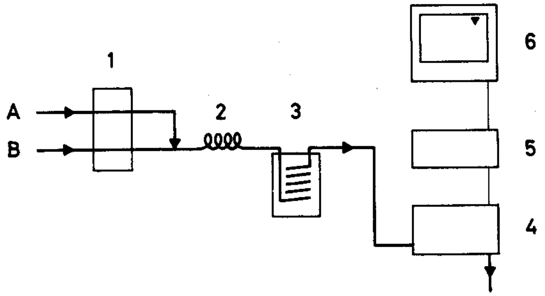


Fig. 1. Outline of the analysis system. (A) Eluate, 0.40 cm^3 min^{-1}; (B) reagent solution (0.11 mM $K_2Cr_2O_7$ in 9.6 M H_2SO_4), 0.90 cm^3 min^{-1}; (1) peristaltic pump; (2) mixing coil; (3) reaction coil of glass in heating bath (120°); (4) photometer; (5) differential amplifier; (6) recorder.

A greater change in absorbance can be obtained if the consumption of chromic acid is determined directly at 440 nm, provided that the oxidation is carried out at low chromic acid concentration. A system based upon this principle is reproduced in Fig. 1. To compensate for the lowered chromic acid concentration the temperature in the reaction bath was increased to 120°. As before[2] silver sulphate was used as a catalyst when difficultly oxidizable species such as succinic acid were present in the sample solution. With this system a very stable base line was recorded at the increased amplification when a carefully mixed solution (eluent + chromic acid) was introduced into the peristaltic pump. Some fluctuations in the base-line were obtained in chromatographic work (see p. 100). These can be ascribed to small fluctuations in the pumping rate which have a greater influence in methods based upon the determination of the reagent consumption, than in those based upon the formation of a coloured compound.

Attempts were made to replace the peristaltic pump by piston pumps. Those furnished with bullet valves gave an uneven flow rate, probably because of the high density and viscosity of the reagent solution. Promising results were obtained with a piston pump with pneumatically operated slide valves (Chromatronix CMP-1L). Unfortunately the standard version contained parts of Delrin which are attacked by the strong sulphuric acid and have to be replaced after a few weeks.

Experiments were also made with the very sensitive diphenylcarbazide method[4]. The application of this method to continuous analysis of the eluate gave a noisier base-line than obtained in the methods above. This can be ascribed to the increasing difficulties in pumping and mixing a great number of liquid streams.

When maleic and fumaric acids are eluted with sodium chloride, chromic acid oxidation cannot be applied. These acids were detected with an u.v. photometer.

All chromatograms were obtained from runs on jacketed columns filled with small beads (10–14 µm) of Dowex 1-X10 resin preconditioned with the eluent applied in the subsequent elution.

The adjusted retention volume which is equal to the observed peak elution volume minus the interstitial volume was determined in runs with single acids and with mixtures, and was calculated in column volumes. Under conditions where Gaussian elution curves with a position independent of the applied sample size were obtained, the adjusted retention volume expressed in column volumes is equal to the volume distribution coefficient D_v. The column volume was determined at the applied temperature (80°) and working pressure (70 bar).

RESULTS AND DISCUSSION

Choice of temperature

The application of high temperature in ion-exchange chromatography has two main advantages. Firstly, the column efficiency can be improved mainly as a result of a more rapid establishment of local equilibrium. Secondly, the flow rate can be increased without excessively high pressures being attained. A third advantage noticed in the previous work on separations in phosphate medium[2] is that the tailing of some elution bands resulting from non-linear exchange isotherms was diminished at high temperature. For this reason 80° was chosen as the working temperature in the present work although the resin deteriorated on prolonged use.

It is well known that the capacity of strongly basic anion-exchange resins decreases in hot aqueous solutions and that part of the quaternary ammonium groups are converted to amino groups[5]. Breakage of cross-linkages and chain-disentanglement effects have also been reported[6]. In chromatographic work in the same eluent a decrease in the D_v values is observed after prolonged use of an anion exchanger. The relative retention is virtually unchanged which means that the separated species can be tentatively identified from the D_v values calculated relative to that of a standard substance ("marker") even if there is a drop in ion-exchange capacity.

A detailed study showed that the situation is more complicated in the systems studied in the present work. The results given in Table I show that after 40 days at 80° and pH 4.0, the D_v values dropped by 6.5 to 14% for different species and that upon prolonged decomposition even larger individual differences were recorded.

Another difficulty encountered at high temperature is that oxidizable material dissolved from the resin is recorded in the analyzer. With the high sensitivity applied in the present work this column bleeding results in changes in the position of the baseline if the flow rate or temperature are changed during the run. Such changes must therefore be avoided. Moreover, start peaks are recorded on the chromatograms (Figs. 5, 6) which are explained by dissolution of material during the time required for loading the column. These peaks can be eliminated by introducing the sample into the eluent stream. The most serious disturbances of this type were observed with an old resin which had been applied at 80° for about one year.

It has been reported that under certain working conditions anion-exchange resins with an aliphatic resin matrix exhibit a better chemical stability than those with a styrene–divinylbenzene matrix[7]. Stability tests carried out with Amberlite XE-258 (a quaternary acrylate-based anion-exchange resin) and a similar resin (kindly supplied by Dr. J. Stamberg, Prague) showed, however, that no advantages were gained with these resins under the applied conditions.

Consequently, it is recommended that the resin be discarded after use for a couple of months at 80°. It is also advisable to use a lower temperature (*e.g.* 50–70°) unless several of the acids which tend to give a serious tailing are present. With some strongly polar acids the separation factors are more favourable at a lower temperature[2] and a lower temperature can therefore be advantageous in many separations of interest in practice.

TABLE I

CHANGES IN THE RECORDED DISTRIBUTION COEFFICIENTS AFTER APPLICATION OF DOWEX 1-X10 AT 80°

Acid	*Decrease (%) in D_v at pH 4.0*		*Decrease (%) in D_v at pH 5.5*
	After 40 days	*After 157 days*	*After 82 days*
Oxalic			13.8
Malonic	8.5	18.9	16.4
Malic	8.8	15.5	11.1
L(+)-Tartaric	8.2	11.8	12.5
Glucaric			11.3
Galactaric			7.8
Fumaric	8.9	23.2	
Maleic	9.3	29.1	23.1
Citraconic	9.4	29.4	24.2
Itaconic	10.5	21.5	15.9
Muconic	9.9	30.5	
Mesoxalic	10.0	23.3	
Oxalacetic[a]	6.5	11.4	13.4
α-Ketoglutaric	9.9	20.6	16.2
Citric	14.0	22.4	
Isocitric			17.0

[a] At the applied temperature oxalacetic acid is rapidly converted to pyruvic acid.

As predicted from the D_v values, some separations at pH 4.0, *e.g.* that of tartaric and malonic acids, became less satisfactory on an aged resin. Other pairs of acids (fumaric–citric and muconic–citraconic acids) were resolved somewhat better after prolonged use of the column, because of a diminished broadening of the elution curves.

Influence of the eluent concentration

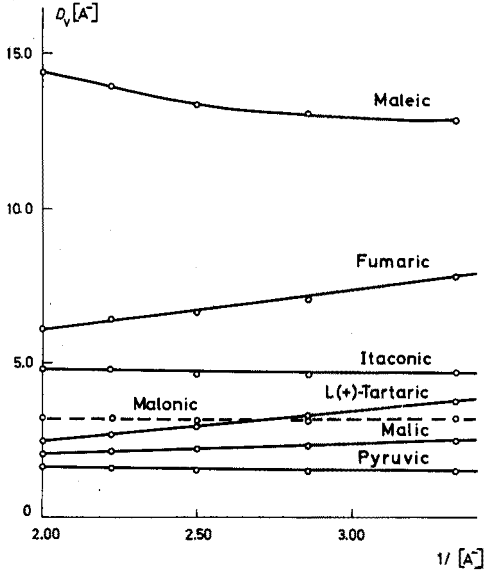
In the elution of monocarboxylic acids with sodium acetate, the D_v values are approximately inversely proportional to the concentration of the eluent[8]. This means that the selectivity coefficients are virtually constant within the range of eluent concentration of interest in practical separations. Corresponding equations for the elution of a dicarboxylic acid, H_2B, with an eluent containing only monovalent anions $[A^-]$ can be easily derived. The following equation holds true for the pH-interval within which the concentration of the undissociated acid can be neglected.

$$D_v = (1-\varepsilon)\left[\frac{k_{HB/A}[A^-]_r/[A^-]}{1+K_2/[H^+]} + \frac{k_{B/A}[A^-]_r^2/[A^-]^2}{1+[H^+]/K_2}\right]$$

Here $k_{HB/A}$ and $k_{B/A}$ represent the selectivity coefficients and K_2 the stoichiometric second dissociation constant of H_2B. The relative interstitial volume is denoted by ε. When the chromatographed species are present in trace amounts and the variations in eluent concentration are small, so that changes in the electrolyte invasion can be neglected, the concentration of A inside the resin $[A]_r$ can be considered constant.

Chromatographic runs carried out with a mixture of six dicarboxylic acids and one monocarboxylic (pyruvic) acid at pH 4.3 and at different phosphate concentrations showed that with six of the acids the deviations from linearity were within the limits of experimental errors (Fig. 2). Only with maleic acid significant deviations were observed. It is interesting to note that this relationship holds true for itaconic and malic acids, although the assumption that the concentration of free acid can be neglected, is not justified with these species. Moreover, the slope of the straight lines is very close to zero for itaconic, malonic and pyruvic acids which means that within the range studied the D_v values are inversely proportional to the eluent concentration. This result was expected for the monocarboxylic acid but not for the two dicarboxylic acids. Numerical calculations based upon the derived equation carried out for itaconic and malonic acids indicate that interactions not accounted for have an influence on the equilibrium uptake. An improved correlation can be obtained by inserting the ratio between the activity coefficients in the external solution and the corrected selectivity coefficients in the above equation, but since the activity coefficient ratio cannot be calculated from available data this would not be of any advantage from a practical point of view. Despite its theoretical limitations the relationship illustrated in Fig. 2 is useful for interpolation and extrapolation purposes.

At pH 4.3 a change in total phosphate concentration resulted in a reversed order of elution of malonic and tartaric acids which is explained by the fact that at this



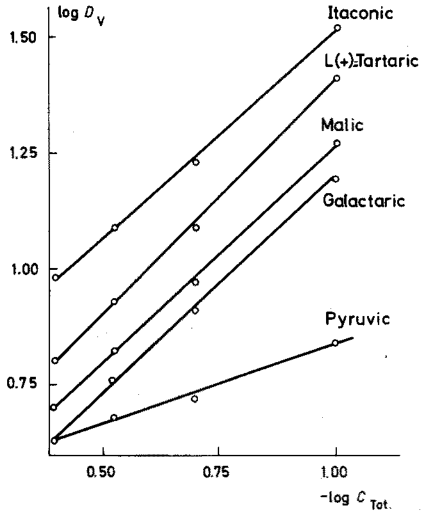


Fig. 2. Relationship between $D_v \cdot [A^-]$ and $1/[A^-]$ for various dicarboxylic acids. Eluent, sodium phosphate; pH, 4.3; flow rate, 7.4 cm min^{-1} (calculated for an empty column); resin bed, 2.6 × 1280 mm.

Fig. 3. Relationship between $\log D_v$ and $\log C_{TOT}$ (total phosphate concentration). Eluent, sodium phosphate; pH, 7.0; flow rate, 9.8 cm min^{-1} (calculated for an empty column); resin bed, 2.6 × 1440 mm. Another batch of resin was used than that referred to in Table II.

pH a larger proportion of dicarboxylic anions are present in the case of tartaric acid and that their uptake is favoured at low eluent concentration.

At pH 7 most species are present mainly as dicarboxylate anions whereas, since both $H_2PO_4^-$ and HPO_4^{2-} ions are present in the solution, the relative amounts of the two species of phosphate ions depend on the total phosphate concentration. For this reason the selectivity coefficients can hardly be considered as constants and no attempt to apply theoretical calculations will therefore be made. Experiments carried out with four dicarboxylic acids at pH 7 showed (Fig. 3) that there exists an approximately linear relationship between log D_v and the logarithm of the total phosphate concentration. The curves are almost parallel and as expected[9] their slopes are much larger than that observed with the monocarboxylic acid (pyruvic acid) included in this series of experiments.

Influence of the column loading

A systematic study of the influence of the column loading was carried out with a mixture of seven acids. The amounts of the mixture applied to the column were varied over a wide range whilst other parameters were kept constant. The adjusted retention volumes calculated in column volumes are reproduced in Fig. 4. At the lowest addition (10–75 μg of each acid) all components were satisfactorily separated and the elution curves were symmetrical or almost symmetrical.

As can be seen from the figure, the retention volume of galactaric acid was unchanged when the added amount was varied within the range 10–1000 μg. The

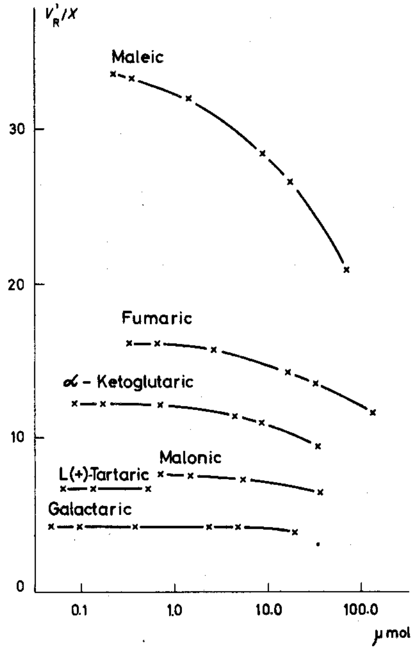


Fig. 4. Influence of the column loading on the adjusted retention volumes of various dicarboxylic acids. The amounts are in logarithmic scale. Eluent, 0.4 M sodium phosphate; pH, 4.0; flow rate, 7.4 cm min^{-1} (calculated for an empty column); resin bed, 2.6 × 1280 mm.

elution curves were symmetrical. These results show that galactaric acid exhibits a linear exchange isotherm over a wide range of concentration and that the adjusted retention volume recorded corresponds to the true D_v value. At the highest addition of the acid mixture a slight decrease in the retention volume was obtained with galactaric acid. This is explained by the fact that in this run the total amount of added acids was so large (9.8% of the exchange capacity of the resin) that an appreciable part of the exchange sites were occupied by anions contained in the sample solution.

With tartaric acid the retention volume was unchanged when the amount of applied acids was increased by a factor of eight. Separate experiments showed that symmetric elution curves with identical D_v values were recorded when the loading was varied within the range 25–1000 μg. These observations as well as similar experiments made with other aldaric acids show that these strongly polar dicarboxylic acids exhibit linear exchange isotherms over a wide concentration range; this means that they can be satisfactorily separated even in milligram amounts provided that the separation factors (ratio of D_v values) differ by about 10% or more.

With malonic acid a tailing was observed when large amounts were applied to the column. In agreement a decrease in the retention volume (4%) was observed when the amount was increased from 75 μg to 600 μg. At higher additions the elution curve overlapped so seriously with that corresponding to tartaric acid that separate peaks were not recorded.

At the lowest additions, α-ketoglutaric and fumaric acids gave symmetrical peaks and constant retention volumes were recorded. With larger additions the tailing became increasingly severe and the retention volumes dropped successively as expected for compounds with non-linear exchange isotherms. The most marked decrease in the retention volume, and at the same time the most pronounced tailing, for large addition was observed with maleic acid.

As mentioned previously the results given in Fig. 4 refer to experiments with a mixture of acids applied to the chromatographic column. Separate experiments with single acids showed that the individual acids behaved similarly which means that the elution of the acids in mixtures is largely determined by the equilibrium distribution of the individual species, and that interactions between various species are of little importance even in those instances where the exchange isotherms are non-linear.

The advantages gained by working with microgram amounts instead of milligram amounts are illustrated in Fig. 5. Comparatively little is gained with acids which appear early on the chromatogram. Mesoxalic acid, which takes an intermediate position, gave a serious tailing when 2.5 mg were applied but only a slight tailing when the amount was lowered by a factor of ten. With the larger amount maleic acid overlaps with muconic acid although the separation factor is equal to 1.19. On the microgram scale the resolution was complete. Muconic and citraconic acids appear in the same elution band with the larger loading and no separation can be traced on the chromatogram. With microgram amounts there is still an overlapping of these acids but the chromatogram can be evaluated for semi-quantitative purposes. The chromatographic run represented in this figure was carried out at pH 4.0, *i.e.* with an eluent containing dihydrogenphosphate as the only eluting ion.

At pH 5.5, *i.e.* with an eluent also containing monohydrogenphosphate ions, a serious tailing was observed on a milligram scale with all species with D_v values above 12 (see also ref. 2). A typical separation of twelve acids achieved on a micro-

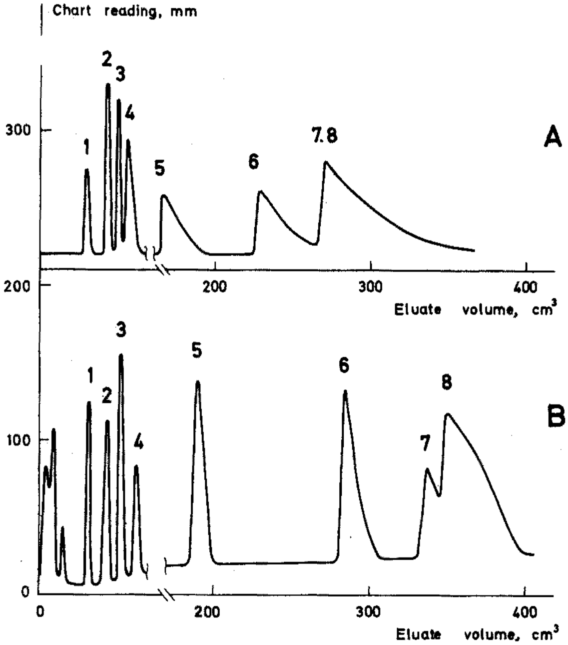


Fig. 5. Separation of a mixture of acids in mg-amounts (A) and in μg-amounts (B). (1) Oxalacetic (pyruvic): (A) 0.5 mg; (B) 25 μg; (2) malic 0.5 mg, 15 μg; (3) L(+)-tartaric 0.5 mg, 20 μg; (4) malonic 1.5 mg, 75 μg; (5) mesoxalic 2.5 mg, 250 μg; (6) maleic 1.0 mg, 40 μg; (7) muconic 1.0 mg, 25 μg and (8) citraconic acid 1.0 mg, 40 μg. Eluent, 0.4 *M* sodium phosphate; pH, 4.0; flow rate, 7.4 cm min^{-1} (calculated for an empty column); resin bed, 2.6 × 1280 mm.

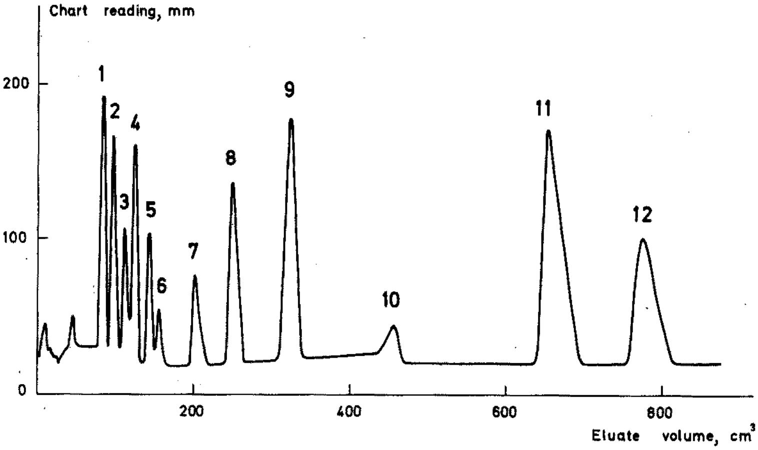


Fig. 6. Separation of 50 μg oxalacetic (pyruvic) (1), 25 μg galactaric (2), 25 μg glucaric (3), 25 μg malic (4), 25 μg L(+)-tartaric (5), 200 μg malonic (6), 250 μg oxalic (7), 50 μg itaconic (8), 50 μg α-ketoglutaric (9), 100 μg isocitric (10), 100 μg maleic (11) and 50 μg citraconic acid (12). Eluent, 0.4 *M* sodium phosphate; pH, 5.5; flow rate, 6.4 cm min^{-1} (calculated for an empty column); resin bed, 4.3 × 1410 mm.

gram scale is reproduced in Fig. 6. No serious tailing was observed and most species were completely separated. Evidently the application of small samples to the chromatographic column eliminates the separation difficulties encountered when large amounts are applied.

A comparison between the chromatogram reproduced in Fig. 5A with that in Fig. 5B and Fig. 6 shows the practical difficulties when work is carried out on a microgram scale. On the latter chromatograms ghost peaks are recorded at low eluate volumes. Moreover, the recorded base-line is unstable. These difficulties are not encountered in work with milligram amounts. The fronting of the peak corresponding to isocitric acid (Fig. 6) was reproducible and is explained by the formation of isocitric lactone during the chromatographic run. In runs at pH 7 no lactone formation was recorded (*cf.* ref. 2).

TABLE II

ADJUSTED RETENTION VOLUME, CALCULATED IN COLUMN VOLUMES, OF DICARBOXYLIC AND TRICARBOXYLIC ACIDS

(Experiments in 0.4 *M* sodium phosphate at pH 4.0, 5.5 and 7.0)

Acid	*pH* 4.0	*pH* 5.5	*pH* 7.0
Oxalic	15.6	8.2	6.8
Malonic	7.8	6.0	4.4
Succinic	4.4	4.9	4.6
Glutaric	4.5	5.6	5.2
Adipic	6.3	7.3	6.8
Pimelic	10.7	12.5	11.9
Suberic			23.6
Azelaic			52.2
Methylmalonic	10.2	7.6	5.0
Methylsuccinic	6.4	6.6	5.1
3,3-Dimethylglutaric	12.4	11.9	7.6
Tartronic	8.2	6.2	5.8
Malic	5.5	4.9	4.5
L(+)-Tartaric (threaric)	6.9	5.7	5.4
Meso-tartaric (erythraric)	5.6	4.9	4.6
Dihydroxytartaric	8.0	6.6	5.8
3-Hydroxy-3-methylglutaric	5.1	5.8	5.8
Glucaric	5.1	4.5	4.8
Galactaric	4.3	3.9	4.1
Fumaric	16.6	12.9	12.5
Maleic	34.6	24.1	7.0
Citraconic	43.1	28.3	7.2
Itaconic	11.2	9.9	8.1
Muconic	41.1	28.8	26.3
Mesoxalic	24.9	19.5	23.6
Oxalacetic (pyruvic)	3.9	3.2	3.7
α-Ketoglutaric	12.6	12.8	13.3
Citric	19.6	16.5	8.7
Isocitric	16.4	17.8	15.1
Isocitric lactone	10.3	9.1	8.3

Distribution coefficients

The volume distribution coefficients (D_v) calculated from a large number of runs with microgram amounts of single acids and various acid mixtures are listed in Table II. The same D_v values were obtained whether single acids or mixtures were chromatographed.

All results determined at pH 4.0 and 5.5 which are listed in the Table were recorded within a short period of time so that the changes in the properties of the resin were negligible. In agreement with the results obtained with milligram quantities of some dicarboxylic acids[2] it is seen that with some species an increase in pH from 4.0 to 5.5 resulted in decreasing retention volumes. The partial transformation of $H_2PO_4^-$ ions into HPO_4^{2-} ions contributes to this displacement in the D_v values and has a greater influence than the competing transformation of uncharged carboxylic acids into monocarboxylate anions and the increased formation of dicarboxylate anions. With other species the latter effects are more important and the D_v values are changed in the opposite direction. Evidently both the dissociation constants of the acids and the affinities of the individual ionic species have an influence. At low pH even the sorption of the non-dissociated carboxylic acid contributes to the D_v value. Non-ionic adsorption of acids is known to occur with monocarboxylic aliphatic acids which are adsorbed in the order of increasing molecular weight[10]. This can be largely ascribed to the hydrocarbon part of the acid. Experiments with monohydroxycarboxylic acids at high pH showed that non-polar interaction forces which increase with lengthening of the hydrocarbon chain contribute markedly to the ion-exchange affinities of monocarboxylate anions[11].

To study the behaviour of dicarboxylate anions without interference from other species experiments were carried out in sodium phosphate at pH 7.0. All values listed in the last column in Table II were determined within a short period of time and are comparable. The runs were made with a resin which had been used much longer than that applied in the experiments carried out at lower pH, and the values are not comparable with those recorded at pH 4.0 and 5.5.

The unsubstituted acids were eluted at pH 7.0 in the order malonic < succinic < glutaric < oxalic = adipic < pimelic < suberic < azelaic acid. The results show that the non-polar interactions contribute markedly to the ion-exchange affinities of the higher homologs of the dicarboxylic acids as well. With the lowest homologs competing factors have a predominant influence, however.

An increased contribution from non-polar interaction forces can be expected when hydrogen is substituted for methyl groups but, as expected and previously established in experiments with monocarboxylic acids[11], the non-polar contributions are larger with straight chain acids than with branched acids. This explains why 3,3-dimethylglutaric acid takes an intermediate position between glutaric and pimelic acids. The slight influence of the introduction of methyl groups into malonic and succinic acids confirms the earlier observation[11] that with lower homologs the non-polar contributions are small. With these species other factors such as size[8] and the acid strength[12] seem to be more important.

For some monocarboxylic acids of similar size correlation has been observed between the acid strength of the parent acid and the anion-exchange affinity. The more strongly an anion takes up a proton, *i.e.* the weaker the parent acid is, the more strongly it should prefer the external solution to the resin phase[12]. This rule can explain the unique position of oxalic acid, which is a much stronger acid than its homologs.

The introduction of hydroxyl groups into the hydrocarbon part of higher monocarboxylic acids results in lowered D_v values, owing to a lowering of the non-polar interaction forces. The increased size and hydration will act in the same direction although with typical hydrophobic species these effects are smaller[11]. On the other hand, the introduction of a hydroxyl group at the carbon atom adjacent to the carboxylic group will increase the acid strength of the parent acid and hence contribute to an increased ion-exchange affinity of the corresponding anion. The fact that the D_v value of tartronic acid is markedly higher than that of malonic acid indicates that the last-mentioned factor is important with ions of small size. With diastereomeric anions this factor should also predominate and as expected L(+)-tartaric acid, which is the stronger acid, is held more strongly than meso-tartaric acid at pH 7.0. The fact that this acid exhibits the same D_v value as the corresponding non-substituted (succinic) and monohydroxy (malic) acids indicates that the influence of the other factors cannot be neglected.

With adipate ions the non-polar contributions to the ion-exchange affinity are obviously important. It was found that the corresponding tetrahydroxyadipic (galactaric and glucaric) acids exhibit much lower distribution coefficients at pH 7.0. This indicates that the combined effect of the elimination of the non-polar contributions and the cooperating factors (increased size and hydration) which tend to push the anions into the external solution is more important than the competing influence of the increased acid strength caused by the presence of the hydroxyl groups. As reported by Mai[13] galactaric acid is a weaker acid than glucaric acid. This offers an explanation for the elution order of the corresponding anions. With glutaric acid the non-polar interactions should be less important. Experiments showed that among the three diastereomeric trihydroxy glutaric acids xylaric acid appears before glutaric acid, whereas ribaric and arabinaric acids are held more strongly. The competition between those forces which tend to increase the ion-exchange affinity and those acting in the opposite direction is reflected also in the position of 3-hydroxy-3-methylglutaric acid which is held more strongly than glutaric acid but less strongly than 3,3-dimethylglutaric acid.

Among the studied ketoacids, oxalacetic acid was decomposed rapidly into pyruvic acid and was therefore eluted at the same position as an authentic sample of pyruvic acid. Mesoxalic and α-ketoglutaric acids exhibited much higher D_v values than malonic and glutaric acids not only in acid but also in neutral medium. This is explained by the fact that the introduction of a keto group results in an increased acid strength.

Additional contributions to the ion-exchange affinity were observed with species containing carbon–carbon double bonds which all appeared later than the corresponding saturated acids. It is interesting that maleate ions are held less strongly than fumarate ions which is in agreement with the order between the dissociation constants for the second proton.

Comparison with other eluents

With the strongly polar dicarboxylic acids the influence of the pH upon the peak position can be roughly predicted from the dissociation constants but with other species such predictions cannot be made. The complicated situation is illustrated by the behaviour of maleic and fumaric acids which at pH 7 are eluted in that order not only in sodium phosphate but also in 1 *M* sodium acetate[1] and in 0.15 *M* sodium chloride[14]. At pH 4 maleic acid is present almost exclusively as hydrogenmaleate ions whereas large amounts of divalent anions are present in the case of fumaric acid. Since as a rule monovalent ions are held less strongly than divalent ions it would be reasonable to assume that the order of elution should be unchanged. The results obtained in sodium phosphate (Table II) showed, however, that the order of elution is reversed when the pH is lowered. Similarly, a reversed order (fumaric < maleic) was obtained in 0.8 *M* sodium acetate and in 0.15 *M* sodium chloride at pH 4. This elution order has previously been observed in experiments with hydrochloric acid as an eluent[15,16].

Experiments carried out at pH 4 with milligram amounts applied to the column showed that both acids exhibited a severe tailing in phosphate medium (*cf.* Fig. 4) whereas in 0.15 *M* sodium chloride at 70°, fumaric acid (eluted between 12 and 20 column volumes) exhibited a severe fronting. Maleic acid gave an extremely wide band recognized only as a small deviation from the base-line at an eluate volume between 30 and 60 column volumes. These puzzling results were reproducible on repacked columns and cannot be ascribed to channelling or similar column effects. At this temperature elution with 0.8 *M* sodium acetate with the addition of acetic acid to obtain pH 4 resulted in symmetric elution peaks with both fumaric (D_v 9.5) and maleic acids (D_v 11.5). In 1 *M* sodium acetate at pH 7 maleic acid gave a symmetric peak (D_v 4.5) whereas fumaric acid gave rise to a tailing peak at 7.7 column volumes[1]. The results indicate that the tailing is depressed by the presence of acetic acid in the eluent. A similar observation was made in experiments with non-polar hydroxymonocarboxylic acids[11]. The concentration of acetic acid inside the resin is higher than that in the external solution, and its presence will depress the non-polar adsorption of other free acids as well as the non-polar contributions to the ion-exchange affinity. The discouraging results obtained with chloride resins indicate that the interactions which give rise to a broadening of the elution curves are strengthened by the presence of chloride ions, and that for this reason chloride media are less favourable than phosphate and acetate media in separations of many organic acids.

Some complications were observed with oxalic acid. Symmetric elution curves were recorded at pH 5.5 and 7.0 when the amounts added to the column were about 250 µg. At pH 4.0 a fronting was obtained even with small amounts added to the column. With milligram amounts a band with two peaks was recorded. It is worth mentioning that similar complications have been encountered when sodium acetate and sodium sulphate were used as eluents. In some practical analyses oxalic acid is present in larger amounts than other dicarboxylic acids and in such instances it is recommended to remove the oxalic acid by precipitation before the chromatographic separation.

When citric acid is present in the solution to be analyzed, it is recommended to carry out the elution at or below pH 4.0. At pH 5.5 a tailing was observed on the microgram scale when the phosphate concentration was 0.4 *M* whereas an almost symmetrical curve was obtained in 0.5 *M* solution. With larger amounts applied to the column double peaks were recorded at this pH.

From a practical point of view it is important that small differences in structure introduce sufficiently large differences in ion-exchange affinity and that by changes in pH advantage can be taken of the differences in dissociation constants of the acids to be separated. The D_v values reported in Table II as well as the correlation between the D_v value and the eluent concentration reproduced in Fig. 2 can be used as a guide in the choice of working conditions. If these values differ by about 12% the compounds can be satisfactorily separated on a column of reasonable length provided that only microgram amounts are applied to the column.

The main advantage of sodium phosphate solutions as eluents compared to acetate media is that the automatic analysis system with chromic acid oxidation can be used to determine acids which are difficult to oxidize, such as succinic and glutaric acids. When acids of these types are to be determined silver sulphate is used as a catalyst. Acetic acid is also oxidized under these conditions and acetate media can only be used with this analysis system when no catalyst is added. Attempts have been made to replace this analytical system by a differential refractometer and this has led to success in separations of milligram amounts for preparative purposes. For analytical purposes the chromic acid oxidation is still superior although, as already mentioned, difficulties are encountered when only microgram amounts are applied to the column.

The financial support of the Swedish Board for Technical Development is gratefully acknowledged.

SUMMARY

Complex mixtures of dicarboxylic acids are separated by anion-exchange chromatography in sodium phosphate and determined automatically by chromic acid oxidation with silver sulphate as catalyst. The influence of column loading, temperature and eluent composition is described. The size of the anions, the acid strength of the parent acid and non-polar contributions have important effects on the retention volume.

RÉSUMÉ

Une méthode d'analyse est proposée pour des mélanges complexes d'acides dicarboxyliques. On procède à une séparation par chromatographie avec échangeur anions en milieu phosphate de sodium. Le dosage se fait ensuite automatiquement par oxydation à l'acide chromique, avec sulfate d'argent comme catalyseur. Divers paramètres ont été examinés.

ZUSAMMENFASSUNG

Komplexe Gemische von Dicarbonsäuren werden durch Anionenaustausch-Chromatographie an Natriumphosphat getrennt und automatisch durch Chromsäure-Oxidation mit Silbersulfat als Katalysator bestimmt. Der Einfluss von Säulenbeladung, Temperatur und Elutionsmittelzusammensetzung wird beschrieben. Die Grösse der Anionen, die Säurestärke der zugehörigen Säure und nichtpolare Beiträge haben einen erheblichen Einfluss auf das Retentionsvolumen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANALYTICAL SEPARATION OF URANIUM AND THORIUM BY LIQUID ANION EXCHANGERS

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(Received 26th May 1971)

Preliminary separation of thorium and uranium from each other and from interfering substances is often required before their determination. The existing techniques based on ion exchange, chromatography, solvent extraction, selective precipitation, etc.[1] present some drawbacks such as poor selectivity or incomplete yield and they often involve time-consuming procedures.

The method described in the present paper, based on liquid anion exchangers, is proposed as an alternative to the above techniques mainly on the ground of its operational simplicity. Uranium in sulfuric acid solutions forms anionic complexes that can be selectively extracted by high-molecular-weight tertiary amines[2] while extraction of thorium in the same system is negligible. Thorium is extracted in high yield from nitrate media by high-molecular-weight quaternary ammonium salts[3]. On this basis uranium and thorium are readily partitioned and separated from a number of interfering ions by successive extractions from sulfate and nitrate media. The analytical measurements are performed in the aqueous phases used for stripping the two elements from the organic phases.

The method has been applied in the analysis of effluents from a laboratory-scale thorium–uranium reprocessing plant and in analysis of low-grade thorium ores, but it can also be used in other cases by introducing minor modifications.

EXPERIMENTAL

Reagents and equipment

Tricaprylamine (TCA), an aliphatic tertiary amine (General Mills, Inc., U.S.A.) diluted in xylene (3% w/v) and equilibrated with 0.1 *M* sulfuric acid, was used to extract uranium. Methyltricaprylammonium chloride (Aliquat-336, General Mills, Inc., U.S.A.), an aliphatic quaternary ammonium salt, diluted in xylene (5% w/v) and converted to the nitrate form by equilibration with 4 *M* nitric acid, was used to extract thorium. All other chemicals used were reagent grade.

Extractions were performed in hand-shaken separatory funnels, a period of 7 min being sufficient to attain equilibrium in all cases.

Spectrophotometric measurements were performed with a Beckman DU spectrophotometer.

Extraction of uranium(VI)

Extraction coefficients for uranium(VI) by the TCA extraction (E_a^0) assume values higher than 100 in the range of 0.05–0.2 M sulfuric acid, and this interval of concentration was used for all the uranium extractions described in this paper. A single extraction was sufficient to transfer more than 99% of the uranium contained in the aqueous phase to the organic phase, when the volume ratio of the organic and aqueous phases was 1:1. Nitrate ions markedly depressed the uranium extraction and had to be eliminated before the TCA extraction, by fuming the solution to a small volume with concentrated sulfuric acid and finally diluting with water to pH 0.5–1. If the nitrate ion concentration was less than 0.03 M, evaporation was unnecessary but in this case two extractions with TCA were required. Back-extraction of uranium into the aqueous phase was achieved by contacting the organic phase with an equal volume of 0.5 M sodium carbonate solution. Uranium in the carbonate solution was determined colorimetrically by means of the sodium carbonate–sodium hydroxide–hydrogen peroxide system[4] when the uranium concentration in the original solution exceeded 10^{-3} M and by means of the dibenzoylmethane–pyridine system for lower concentrations[5].

Extraction of thorium

Maximum extraction coefficients ($E_a^0 \simeq 50$) for thorium were obtained in the 2–5 M nitric acid concentration range. In the present work aqueous 4 M nitric acid solutions were used. Complete extraction of thorium into the organic phase was obtained by two equilibrations with equal volumes of organic and aqueous phases. Back-extraction into the aqueous phase was obtained by equilibrating the resulting organic phase twice with equal volumes of 3 M hydrochloric acid. Thorium in the aqueous phase was determined colorimetrically with thoron[6] or, for sufficiently high concentrations, by titration with EDTA in the presence of alizarin S as indicator[7].

Recommended procedure for separation of uranium and thorium

To separate uranium from thorium, uranium is first extracted from sulfate media with TCA; under these conditions extraction of thorium is negligible ($E_a^0 < 0.1$).

Adjust the original solution to 0.05–0.2 M in sulfuric acid and extract uranium with an equal volume of 3% (w/v) TCA in xylene. Wash the organic phase with a half volume of 0.1 M sulfuric acid and add this wash solution to the aqueous phase containing unextracted thorium. Adjust the resulting solution to 4 M in nitric acid and extract thorium with 5% (w/v) Aliquat-336 in xylene, using two equilibrations with equal volumes of the two phases. Sulfuric acid concentrations below 0.2 M in the aqueous phase do not affect the extraction of thorium. Finally, back-extract uranium and thorium and determine them as described above.

Notes. If only the determination of thorium is required, uranium separation is unnecessary. Actually uranium is partially extracted by Aliquat-336 from 4 M nitric acid solutions ($E_a^0(\mathrm{U}) \simeq 2$)[8] but it is only very slightly back-extracted into the 3 M hydrochloric acid phase ($E_a^0(\mathrm{U}) \simeq 30$) used as the stripping solution for thorium ($E_a^0(\mathrm{Th}) < 2 \cdot 10^{-3}$)[9]. Analytical separation of thorium from uranium is possible for molar ratios of uranium to thorium up to 100. The trace amounts of uranium back-extracted by 3 M hydrochloric acid do not interfere with the spectrophotometric determination.

RESULTS

In Table I the results of a series of separation tests obtained by the recommended procedure are reported.

The effects of the presence of foreign ions in the initial solution on the determination of uranium and thorium were also investigated. A summary of the results is presented in Table II.

TABLE I

SEPARATION OF URANIUM(VI) AND THORIUM(IV)
(Volume of the initial sample 25 ml)

Present (mg/ml)		*% Found*[a]	
U(VI)	*Th*	*U(VI)*	*Th*
2.5	2.5	100.0	98.8
0.8	0.8	99.5	98.5
0.8	0.2	99.5	99.8
0.2	0.8	98.6	98.0
0.2	0.2	98.8	98.2

[a] Average of 3 extractions and determinations.

TABLE II

EFFECTS OF FOREIGN IONS ON THE DETERMINATION OF URANIUM AND THORIUM
(Initial solution: volume 25 ml, U(VI) 0.8 mg ml^{-1}, Th 0.8 mg ml^{-1}, H_2SO_4 0.1 *M*)

Ion	*Highest level studied without interference (mg added)*	*Ion*	*Highest level studied without interference (mg added)*
Lithium	500	Nickel	100
Sodium	500	Cobalt	100
Potassium	500	Manganese(II)	100
Magnesium	100	Titanium(IV)	20
Copper(II)	100	Chromium(III)	100
Silver	100	Chromium(VI)[a]	100
Zinc	100	Zirconium(IV)[b]	10
Cadmium	100	Molybdenum(VI)[b,c]	100
Mercury(II)	100	Tungsten(VI)[d]	100
Aluminum	100	Vanadium(V)[a]	20
Thallium(I)	100	Bismuth(III)[f]	10
Lanthanum	100	Chloride[e]	150
Cerium(IV)	100	Fluoride[e,f]	25
Yttrium	100	Nitrate[e]	25
Iron(III)[a]	100	Phosphate[e,f]	400

[a] Reduced by hydroxylamine sulfate before TCA extraction.

[b] Strongly extracted by TCA but not interfering with the spectrophotometric determination in the Na_2CO_3–$NaOH$–H_2O_2 system.

[c] 0.2 *M* H_2SO_4.

[d] 0.05 *M* H_2SO_4.

[e] Higher quantities interfere by decreasing the extraction of uranium.

[f] Thorium precipitation.

TABLE III

ANALYSIS OF SAMPLES FROM AN EXPERIMENTAL LABORATORY-REPROCESSING PLANT

Recommended procedure Found ($g\ l^{-1}$)		*LaF_3 coprecipitation Found ($g\ l^{-1}$)*	
Uranium	*Thorium*	*Uranium*	*Thorium*
13.40	265.5	13.45	267.0
103.60	246.5	104.50	246.0
1.60	37.0	1.62	37.2
1.30	31.1	1.33	31.1
1.25	0.05	1.23	0.05
1.12	< 0.002	1.11	< 0.002
< 0.002	62.4	< 0.002	62.7
< 0.002	35.6	< 0.002	35.6
< 0.002	0.75	< 0.002	0.70
< 0.002	3.55	< 0.002	3.50

TABLE IV

ANALYSIS OF LOW-GRADE THORIUM ORES

Sample	*% Thorium*	
	Recommended procedure	*Reference* 13
1	0.24	0.25
2	0.17	0.17

In Table III the results obtained for actual samples by means of the recommended procedure are reported; the results obtained for the same samples by an established procedure are given for comparison. The latter method was an accurate analytical technique based on separation of thorium from uranium by coprecipitation with lanthanum fluoride[10] followed by extraction of thorium with mesityl oxide[11] and determination with thoron, and extraction of uranium by TBP and direct determination in the organic phase with dibenzoylmethane[12]. These samples originated in a laboratory-scale uranium–thorium reprocessing plant and, besides thorium and uranium, contained 0.05 *M* aluminum, 0.03 *M* iron, 0.01 *M* chromium, 0.005 *M* nickel, 0.001 *M* manganese, and 0.08–7.0 *M* nitric acid.

Results obtained for low-grade thorium ores are reported in Table IV, in which the results obtained by the method of Banks and Byrd[13] are given for comparison.

The authors wish to thank Mr. F. Barachini for valuable laboratory assistance.

SUMMARY

A liquid–liquid extraction separation of uranium and thorium from each other and from interfering ions is described. Uranium is separated from sulfate solutions with a tertiary amine (tricaprylamine) and thorium from nitrate solutions with a quaternary ammonium salt (Aliquat-336). The method has been successfully applied to the analysis of effluents from a miniature reprocessing plant and to the determination of thorium in low-grade ores.

RÉSUMÉ

On décrit une méthode de séparation par extraction liquide–liquide du thorium et de l'uranium d'avec des ions gênants. L'uranium est séparé en solution sulfate à l'aide d'une amine tertiaire (la tricaprylamine) et le thorium en solution nitrate au moyen d'un sel d'ammonium quaternaire (Aliquat-336). Cette méthode a été appliquée avec succès à l'analyse d'effluents et au dosage du thorium dans des minerais.

ZUSAMMENFASSUNG

Es wird eine Flüssig–Flüssig-Extraktionstrennung von Uran und Thorium voneinander und von störenden Ionen beschrieben. Uran wird aus Sulfatlösungen mit einem tertiären Amin (Tricaprylamin) und Thorium aus Nitratlösungen mit einem quaternären Ammoniumsalz (Aliquat-336) abgetrennt. Die Methode wurde mit Erfolg auf die Analyse von Abwässern aus einer Miniatur-Wiederaufarbeitungsanlage und auf die Bestimmung von Thorium in Erzen mit geringem Gehalt angewendet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF THORIUM IN PLUTONIUM METAL BY LINEAR SWEEP OSCILLOGRAPHIC POLAROGRAPHY*

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(Received 13th April 1971)

The analytical chemistry of thorium up to 1961 has been well documented[1,2]. Since that time, very many methods for the determination of thorium have been reported, but little seems to have been done on the polarography of thorium. Sancho *et al.*[3] have investigated the polarographic behavior of thorium in dimethyl sulfoxide media.

Superchrome Garnet Y has been used by Saylor and Castor to develop an amperometric procedure for determination of fluoride by means of its aluminum complex[4]. This dye has also been used in the polarographic determination of aluminum, the aluminum–Superchrome Garnet Y complex being reduced[5], and in an analogous determination of gallium[6]. Several papers have appeared describing the use of Superchrome Garnet Y (SGY) for the determination of aluminum, gallium, and indium[7-12].

This paper describes a polarographic determination of thorium in plutonium metal based on anion exchange for preliminary separation of plutonium, and then reduction of the thorium–SGY complex.

EXPERIMENTAL

Apparatus

A Davis Differential Cathode Ray Polarotrace, Type A-1660 (Southern Analytical, Ltd., Camberley, England) equipped with an electrode stand and a constant-temperature water bath, was used. This instrument has a voltage sweep rate of 0.25 V sec^{-1}, a sweep time of 2 sec and a delay period of 5 sec. All polarographic measurements were made at 30°. A polarographic cell with a mercury pool anode was used throughout the investigation. A single 15-cm long capillary was used for all measurements. The $m^{\frac{2}{3}} t^{\frac{1}{6}}$ value, obtained at zero voltage in a buffer solution containing $1.86 \cdot 10^{-3}$ *M* SGY, was 1.16.

The pH values of the solutions were measured with a Sargent Model DR pH

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* Work performed under U.S. Atomic Energy Commission Contract AT(29-1)-1106.

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meter and a glass electrode. The pH was adjusted with perchloric acid or sodium hydroxide.

Reagents

Stock solutions of thorium perchlorate were prepared by dissolving thorium nitrate ("Baker Analyzed" Reagent) in water and taking the solution to incipient dryness. The thorium salt was dissolved in 2.5 *M* perchloric acid and diluted to volume with water. The perchloric acid concentration was *ca.* 0.5 *M*. The thorium solutions were standardized as described by Körbl and Přibil[13].

The sodium salt of Superchrome Garnet Y (Keystone Aniline and Chemical Company, Chicago, U.S.A.) was purified by a double recrystallization from ethanol. A $10.0 \cdot 10^{-3}$ *M* solution of the dye was prepared by dissolving the purified dye in water, and standardized by conductometric titration against a standard aluminum solution which was buffered at pH 3.4 with acetate.

A boric acid–sodium perchlorate buffer was prepared by combining 500 ml of 0.50 *M* boric acid solution and 500 ml of 0.50 *M* sodium perchlorate solution.

A wash solution was prepared by adjusting 1.5 l of water to pH 8.00 with a dilute solution of sodium hydroxide.

The ion-exchange resin used was Dowex 1-X2, 100–200 mesh, chloride form. All other chemicals were reagent grade, and the solutions were prepared in a normal manner.

Safety precautions

Extreme care must be exercised in the handling of plutonium because of its toxicity. All work with plutonium was performed in a glovebox. The solutions containing the separated thorium were analyzed polarographically in a well ventilated hood.

Preparation of ion-exchange columns

The ion-exchange columns used were of conventional design, being of 2.2 cm internal diameter and *ca.* 35 cm long with a flared 10-cm long top of 3.5 cm internal diameter. A coarse porosity, sintered glass disk supported the resin bed which was 25 cm high. The resin was pretreated by washing with 150–200 ml of concentrated hydrochloric acid daily before use.

No plutonium was allowed to remain on the resin overnight because of the formation of gas bubbles[14].

Procedure

Select a weight of plutonium metal such that 0.05–2.00 mg of thorium is present. Dissolve in a 100-ml beaker with a minimum volume of 6 *M* hydrochloric acid, and then add 1 ml of concentrated nitric acid and 1 ml of 30% hydrogen peroxide. Evaporate to incipient dryness under an infrared lamp. Wash the beaker and watch glass with a minimum volume of concentrated hydrochloric acid, and warm on a hot plate to insure complete dissolution. Cool, and again wash the beaker and watch glass with a minimum volume of concentrated hydrochloric acid. Transfer the solution to the ion-exchange column for separating the plutonium from the thorium and elute at 3 ml min^{-1} with concentrated hydrochloric acid. Collect a total of 60 ml in a 100-ml beaker.

Place this eluate under an infrared lamp, and evaporate to incipient dryness. Wash the beaker and watch glass with a minimum volume of water. Add 1 drop of concentrated perchloric acid, and warm the solution on a hot plate. Cool, and add 5 ml of SGY solution followed by 5 ml of the borate buffer solution. Adjust the pH to 8.00±0.02, and transfer the solution to a 25-ml volumetric flask with the pH 8.00 wash solution. Allow to stand for 1 h at room temperature to permit complete formation of the thorium–SGY complex. Transfer a 5-ml portion of the solution to an electrolysis cell, and remove oxygen by passing purified nitrogen gas through the solution for 10 min. Read the peak current at −0.67 V *vs.* a mercury pool, which corresponds to the reduction peak of the uncomplexed SGY. The reduction peak of the thorium–SGY complex is measured at −0.80 V *vs.* the mercury pool.

RESULS AND DISCUSSION

Effect of pH

The effect of pH on the peak currents was studied with solutions which were $2.53 \cdot 10^{-4}$ *M* in thorium and $1.86 \cdot 10^{-3}$ *M* in SGY, and contained 5 ml of the boric acid–sodium perchlorate buffer. Plots of the peak currents *versus* the pH (Fig. 1) showed that below pH 4.0 the unchelated dye peak and the thorium chelate peak merge to form one large rounded peak at *ca.* −0.75 V *vs.* Hg pool. At pH 2.0 and below no peaks are formed; above pH 9.0 only the unchelated dye peak appears.

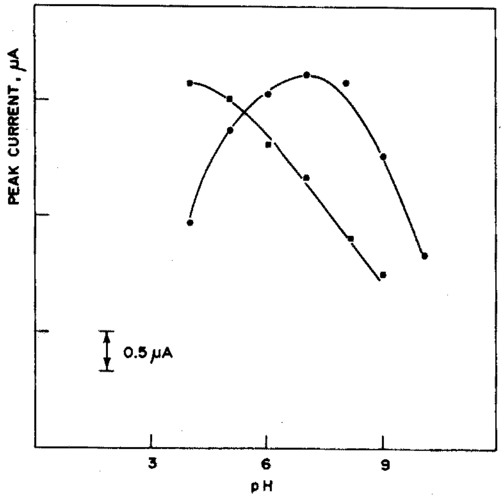

Fig. 1. Variation of peak currents with pH. $2.53 \cdot 10^{-4}$ *M* thorium; $1.86 \cdot 10^{-3}$ *M* Superchrome Garnet Y; 5 ml of buffer per 25 ml. (●) Peak current of uncomplexed SGY; (■) peak current of thorium–SGY complex.

A change of one pH unit in the pH range 7.5±0.5 would cause an error of less than 2% in the thorium results if the uncomplexed SGY peak were used, whereas, if the thorium–SGY peak were used, a change of one pH unit would cause an error in excess of 20%. It was, therefore, obvious that very close pH control would be necessary if both peaks were to be used for the thorium analysis; this was accomplished by using boric acid–sodium perchlorate buffer, which, under the experimental conditions reported here, has its maximum buffering capacity at pH *ca.* 8–9. To obtain the maximum current for the thorium–SGY peak and to use the maximum buffering capacity of the buffer, a value of pH 8.00 ± 0.02 was chosen. The error in the thorium results caused by a ±0.02 pH unit variation would be less than 2% for the thorium–SGY peak, and essentially nil for the uncomplexed SGY peak.

Attempts to use other buffer systems failed. A sodium citrate–sodium perchlorate system produced only one peak. The peak shape did indicate that there might be a thorium–SGY complex formed, but its peak potential was too near the peak potential of the SGY. A sodium acetate–sodium perchlorate system also produced only one peak; there was no indication of a thorium–SGY complex having been formed. Florence[9] has stated that acetate masks thorium. A third buffer system which contained sodium phosphate and sodium perchlorate produced two peaks, but the peaks were erratic, probably because of the formation of a thorium phosphate precipitate[1].

Equilibration time

The time required for the complete formation of the thorium–SGY complex was studied (Fig. 2). The equilibration time was measured from the time the solution was diluted to volume. Complete formation of the complex was not achieved at room temperature until 50 min had elapsed.

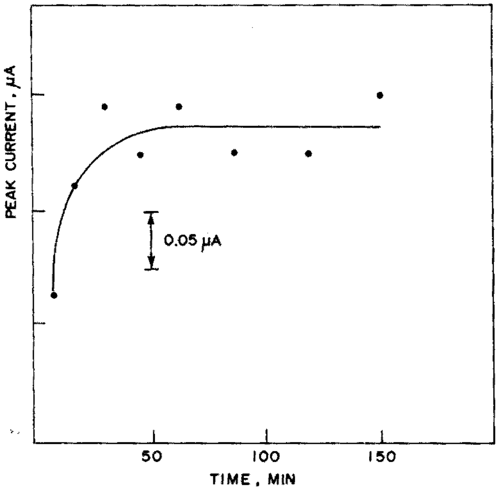

Fig. 2. Equilibration time for the thorium–SGY peak current. $2.11 \cdot 10^{-4}$ *M* thorium; $1.86 \cdot 10^{-3}$ *M* Superchrome Garnet Y; 5 ml of buffer per 25 ml; pH 8.00 ± 0.02.

Calibration procedure

The calibration curve for thorium was prepared by transferring an appropriate portion of a standard thorium solution into a 100-ml beaker containing 5 ml of 6 *M* hydrochloric acid; 1 ml of concentrated nitric acid and 1 ml of 30% hydrogen peroxide

TABLE I

PEAK CURRENTS AS FUNCTIONS OF THE THORIUM CONCENTRATION
($1.86 \cdot 10^{-3}$ *M* Superchrome Garnet Y, 5 ml of buffer per 25 ml, pH 8.00±0.02)

Th concn. (10^{-4} *mole* l^{-1})	*SGY* i_p (μA)	*Thorium–SGY complex*	
		i_p (μA)	$i_p/[Th]$ (μA *mmole*$^{-1}$ l^{-1})
0.634	14.3	0.55	8.7
0.845	13.4	0.71	8.4
1.06	12.4	0.91	8.6
1.27	10.8	1.11	8.8
1.69	8.82	1.52	9.0
2.11	6.92	1.89	9.0
2.53	5.42	2.27	9.0
2.96	2.77	2.49	8.4
3.38	0.72	2.91	8.6

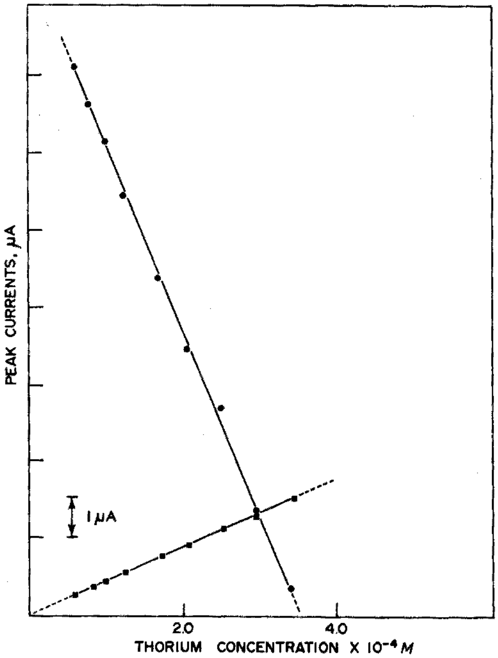

Fig. 3. Variation of peak currents with varying thorium concentration. $1.86 \cdot 10^{-3}$ *M* Superchrome Garnet Y; 5 ml of buffer per 25 ml; pH 8.00±0.02. (●) Peak current of uncomplexed SGY; (■) peak current of thorium–SGY complex.

were then added and the above procedure was followed. Thirty-six thorium solutions of nine different concentrations were prepared and polarographed. The mean results (Table I) show that the peak current of the uncomplexed SGY and the peak current of the thorium–SGY complex are both proportional to the thorium concentration at pH 8.00 ± 0.02. The relative standard deviation for all polarograms at all concentrations was 4.52 % for the thorium–SGY complex peak, and 4.88 % for the uncomplexed SGY peak.

Figure 3 shows the variations of the peak currents of the thorium–SGY complex and the uncomplexed SGY as functions of the thorium concentration. The proportionality between the thorium concentration and the uncomplexed SGY peak current can be clearly seen.

The calibration data covered the range $6.34 \cdot 10^{-5}$–$3.38 \cdot 10^{-4}$ *M* thorium.

TABLE II

PEAK CURRENTS AS FUNCTIONS OF THE LOWER THORIUM CONCENTRATION

($3.72 \cdot 10^{-4}$ *M* Superchrome Garnet Y, 5 ml of buffer per 25 ml, pH 8.00 ± 0.02)

Th concn. (10^{-4} *mole* l^{-1})	*SGY* i_p (μA)	*Thorium–SGY complex*	
		i_p (μA)	$i_p/[Th]$ (μA *mmole*$^{-1}$ l^{-1})
0.845	5.80	0.26	30.5
1.69	4.90	0.56	33.4
2.11	4.60	0.73	34.7
2.53	4.34	0.82	32.3
4.22	2.82	1.38	32.6

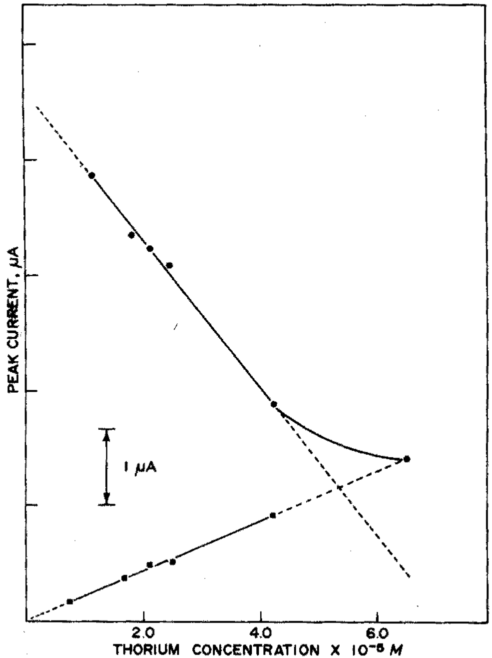

Fig. 4. Variation of peak currents with lower varying thorium concentration. $3.72 \cdot 10^{-4}$ *M* Superchrome Garnet Y; 5 ml of buffer per 25 ml; pH 8.00 ± 0.02. (●) Peak current of uncomplexed SGY; (■) peak current of thorium–SGY complex.

Below $6.34 \cdot 10^{-5}$ *M* thorium(IV), the large excess of SGY in the cell caused problems in reading the thorium–SGY complex peak. Therefore, to lower the thorium concentration limit, a second calibration curve was prepared as described above, except that the SGY concentration was $3.72 \cdot 10^{-4}$ *M*. Twenty thorium solutions of five different concentrations in the concentration range $8.45 \cdot 10^{-6}$–$4.22 \cdot 10^{-5}$ *M* were polarographed. The mean results (Table II) show that the peak currents of the uncomplexed SGY and of the thorium–SGY complex were again both proportional to the thorium concentration at pH 8.00 ± 0.02. The relative standard deviation for all 20 polarograms was 5.22% for the thorium–SGY complex peak and 5.13% for the uncomplexed SGY peak.

Figure 4 shows the variations of the peak currents of the thorium–SGY complex and the uncomplexed SGY as functions of the thorium concentration. The "tailing-off" of the uncomplexed SGY calibration curve occurs when there is insufficient uncomplexed SGY present to shift the equilibrium towards the formation of the thorium–SGY complex.

An attempt was made to prepare a third calibration curve with $7.45 \cdot 10^{-5}$ *M* SGY, and thorium concentrations of $6.34 \cdot 10^{-6}$ *M* and less. This failed because the thorium–SGY peaks were not stable, and the change in height of the more stable uncomplexed SGY peak was judged to be too small to be significant.

Analysis of standard thorium solutions

Analysis of 27 thorium solutions, covering the range 2–80 μg Th ml^{-1} without plutonium, by measurement of the thorium–SGY peak, showed recoveries ranging from 94.1% to 106.0% with an average of 100.6%. Analysis of 21 thorium solutions, covering the same range, by measurement of the uncomplexed SGY peak, showed recoveries ranging from 95.9% to 105.1% with an average of 100.2%.

Effect of diverse ions

The effect of 32 diverse ions on the recovery of thorium was investigated in solutions which were $4.22 \cdot 10^{-5}$ *M* in thorium, $3.72 \cdot 10^{-4}$ *M* in SGY, 0.05 *M* in boric acid and 0.05 *M* in sodium perchlorate at pH 8.00±0.02. The results (Table III) indicate that only 11 of the 32 diverse ions do not interfere. However, 16 of the interfering ions are removed during the ion-exchange separation of the thorium from the plutonium, remaining on the column along with the plutonium.

Chromium, manganese, nickel, and lead, of the remaining six interfering ions, can be removed by mercury cathode electrolysis, with a semi-micro electrolysis cell[15]. The aluminum interference can be removed by precipitating the thorium as the fluoride, with lanthanum as carrier; the aluminum remains in solution as an aluminum fluoride complex.

Recovery of thorium in the presence of plutonium

The effect of plutonium on the determination of thorium was examined by spiking plutonium solutions with standard thorium solutions. Fourteen solutions containing 100–500 mg of plutonium were spiked so that the final thorium concentration ranged from 2 to 80 μg ml^{-1}. These solutions were taken through the sample preparation procedure and analyzed. The recovery ranged from 94.6 to 104.5% with an average of 99.3%.

TABLE III

INVESTIGATION OF DIVERSE IONS
(An error of < 6% is regarded as insignificant)

Ion added	*μg ion per 25 ml*	*Recovery of Th (%)*	
		SGY	*Th–SGY*
Ag(I)	1000	—[a]	—[a]
Al	1000	164	52
	25	—[a]	—[a]
Ba	1000	—[a]	—[a]
Ca	1000	—[a]	—[a]
Cd	1000	<10	—[c]
	10	—[a]	—[a]
Ce(III)	1000	—[a]	—[a]
Co(II)	1000	59	—[c]
	25	—[a]	—[a]
Cr(III)	1000	49	21
	25	—[a]	—[a]
Cu(II)	1000	68	356
	25	—[a]	—[a]
Fe(III)	1000	143	276
	30	—[a]	—[a]
Ga(III)	1000	188	39
	25	—[a]	—[a]
Ge	1000	—[a]	—[a]
Hg(II)	1000	141	58
	250	—[a]	—[a]
La	1000	—[a]	—[a]
Li	1000	—[a]	—[a]
Mg	1000	—[a]	—[a]
Mn(II)	1000	—[b]	32
	50	—[a]	—[a]
Mo(VI)	1000	31	—[c]
	250	—[a]	—[a]
Ni(II)	1000	—[b]	<10
	10	—[a]	—[a]
Np(VI)	1000	677	246
	350	—[a]	—[a]
Pb(II)	1000	<10	53
	260	—[a]	—[a]
Sb(V)	1000	72	244
	70	—[a]	—[a]
Si	1000	—[a]	—[a]
Sn(IV)	1000	—[d]	—[d]
	5	—[a]	—[a]
Sr	1000	—[a]	—[a]
Ti(IV)	1000	75	—[b]
	100	—[a]	—[a]
U(VI)	1000	—[b]	67
	10	—[a]	—[a]
V(V)	1000	—[b]	780
	25	—[a]	—[a]
W(VI)	1000	74	—[b]
	25	—[a]	—[a]
Y	1000	—[a]	—[a]
Zn	1000	—[b]	85
	10	—[a]	—[a]
Zr	1000	—[b]	247
	100	—[a]	—[a]

[a] Error < ±6%. [b] No peak formed at −0.67 V *vs.* Hg pool, indicating no excess of SGY. [c] No peak formed at −0.80 V *vs.* Hg pool. SGY blocked by diverse ion forming stronger complex than Th–SGY. [d] Ill-defined peak.

SUMMARY

The polarographic determination of thorium in plutonium is described. The plutonium is separated by anion exchange in a chloride medium, and the thorium is determined in the eluate by means of Superchrome Garnet Y in a buffered solution at pH 8.0. The thorium concentration range in the polarographed solutions is $8.5 \cdot 10^{-6}$–$3.4 \cdot 10^{-4}$ *M*. The average recovery of thorium is 99.3% with a relative standard deviation of 5.2%. Of the 32 diverse ions investigated only aluminum, chromium, manganese, nickel, and lead cause significant interference.

RÉSUMÉ

On décrit un dosage polarographique du thorium dans le plutonium. On procède à une séparation sur échangeur d'anions, en milieu chlorure; le thorium est dosé dans l'éluat au moyen de Superchrome Garnet Y en solution tampon à pH 8.0. Le domaine de concentrations de la solution à polarographier va de $8.5 \cdot 10^{-6}$ à $3.4 \cdot 10^{-4}$ *M*. Le rendement moyen du thorium est de 99.3% avec une déviation standard relative de 5.2%. Parmi les 32 ions examinés, seuls aluminium, chrome, manganèse, nickel et plomb interfèrent notablement.

ZUSAMMENFASSUNG

Es wird die polarographische Bestimmung von Thorium in Plutonium beschrieben. Das Plutonium wird durch Anionenaustausch in einem Chloridmedium abgetrennt und das Thorium im Eluat mittels Superchrome Garnet Y in einer gepufferten Lösung bei pH 8.0 bestimmt. Der Thoriumkonzentrationsbereich in den polarographierten Lösungen ist $8.5 \cdot 10^{-6}$–$3.4 \cdot 10^{-4}$ *M*. Der erfasste Anteil des Thoriums ist im Mittel 99.3% bei einer relativen Standardabweichung von 5.2%. Von den 32 untersuchten Ionenarten stören nur Aluminium, Chrom, Mangan, Nickel und Blei erheblich.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ETUDE POTENTIOMETRIQUE ET SPECTROPHOTOMETRIQUE DE LA COMPLEXATION DES IONS FERRIQUES PAR L'ACIDE SULFO-5-SALICYLIQUE

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(Reçu le 5 juin 1971)

Dans le cadre d'une étude générale des complexes mixtes formés par les ions ferriques nécessitant la connaissance exacte des constantes de stabilité des espèces simples, nous avons été amenés à préciser les données relatives au système Fe(III)–acide sulfo-5-salicylique (H_3ASS).

Bien que les complexes formés dans ce système aient été étudiés par de nombreux auteurs[1-7], une étude critique des résultats obtenus montre que la concordance entre les différentes valeurs des constantes de stabilité déterminées est souvent médiocre et que les conditions expérimentales telles que force ionique et température ne sont pas toujours fixées avec rigueur. L'hydrolyse notable des ions ferriques en solution aqueuse, même fortement acide, est certainement une cause fréquente de ces écarts. D'autre part, les complexes formés dans ce système étant fortement colorés, il faut noter que la plupart des études antérieures ont été effectuées par des méthodes spectrophotométriques souvent moins précises que les méthodes potentiométriques classiques.

Nous avons donc cru devoir reprendre cette étude par une méthode protométrique très précise qui nous a permis de déterminer les constantes de stabilité ionique $\beta_n = [\mathrm{Fe(ASS)}_n]/[\mathrm{Fe}]\,[\mathrm{ASS}]^n$.

D'autre part, l'application d'une méthode spectrophotométrique trichrome permet de vérifier les résultats trouvés notamment en ce qui concerne les différentes zones d'existence des espèces $[\mathrm{Fe(ASS)}_n]$.

Toutes nos mesures furent effectuées à la température de 25° ±0.1°, en milieu de force ionique 0.5 *M* maintenue constante par du nitrate de sodium.

TECHNIQUES EXPÉRIMENTALES

Spectrophotométrie

Le principe des déterminations consiste à mesurer simultanément avec le pH, au cours d'une neutralisation progressive par la soude, l'absorption lumineuse de solutions contenant l'ion métallique, l'agent chélatant, de l'acide nitrique et du nitrate de sodium. Grâce à une pompe péristaltique, la solution circule en permanence de la cellule "potentiométrique" RMO 6 Tacussel thermostatée, à la cellule "spectrophotométrique" qui est une cuve à circulation de 1 cm d'épaisseur. Nous enregistrons à

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l'aide d'un spectrophotomètre Beckman type DK 2A le spectre d'absorption de la solution dans le domaine 385–555 nm pour les différentes valeurs du pH.

Potentiométrie

Les mesures de pH sont faites grâce à un compensateur Metrohm E 388 à 0.2 mV près.

Les étalonnages sont effectués:

soit par deux tampons; respectivement biphtalate de potassium 0.05 *M* (pH = 4.005) et borax 0.05 *M* (pH = 9.196);

soit pour les régions de forte acidité pour lesquelles les mesures sont toujours délicates, au moyen d'un titrage "acide sans base", c'est à dire, en ajoutant une solution d'acide nitrique et de nitrate de sodium à la force ionique $\mu = 0.5$ dans une quantité donnée de $NaNO_3$ à la même force ionique.

On obtient alors directement les variations de la force électromotrice en fonction de la concentration des ions hydrogène libres, selon la loi de Nernst.

Réactifs

Nous avons utilisé le nitrate ferrique commercial, $Fe(NO_3)_3 \cdot 9\ H_2O$ p.a. en préparant des solutions acides de concentration $[Fe(III)] \simeq 10^{-2}$ *M*, $[HNO_3] \simeq 10^{-1}$ *M*. Dans ces conditions on obtient une solution incolore où le fer est dosé de façon classique par le bichromate de potassium.

Un problème important réside dans la détermination de l'acidité libre de telles solutions. Après de nombreux essais (résines échangeuses d'ions, dosage des nitrates) nous avons retenu une méthode proposée par Gustafson et Martell[8] consistant en un titrage potentiométrique de solutions contenant des quantités équimoléculaires d'ions ferriques et du sel disodique de l'E.D.T.A. La différence entre la quantité de base nécessaire pour atteindre le point d'inflexion correspondant à la formation du chélate ferrique de l'E.D.T.A. et la quantité calculée pour neutraliser les protons libérés par le coordinat permet d'atteindre la quantité d'acide libre présente.

Enfin pour déterminer le point d'inflexion avec le maximum de précision nous avons appliqué la méthode de Gran[9] à la portion de courbe située avant le saut de pH.

L'acide sulfosalicylique était le dihydrate commercial p.a. utilisé sans purification supplémentaire.

LES CONSTANTES D'IONISATION

Avant d'aborder l'étude de la chélation proprement dite, il était nécessaire de déterminer avec précision, pour nos conditions expérimentales, les constantes d'ionisation $K_n^H = [H_{n-1}ASS]\ [H]\ [H_nASS]$ du coordinat envisagé. Le groupement sulfonique de l'acide sulfosalicylique se comportant comme un acide fort, nous négligerons K_3^H et nous ne tiendrons compte que des deux constantes K_2^H et K_1^H. Les courbes de neutralisation par la soude de solutions 0.5 *M* en $NaNO_3$ et $1.985 \cdot 10^{-2}$, $1.389 \cdot 10^{-2}$ et $0.993 \cdot 10^{-2}$ *M* en acide sulfosalicylique permettent de tracer la courbe représentant le nombre moyen $\bar{p}$ de protons liés par coordinat en fonction du pH. L'exploitation de cette courbe conduit aux valeurs $pK_1^H = 11.57$ et $pK_2^H = 2.40$. Cependant afin d'utiliser un nombre maximum de données, nous avons aussi calculé ces deux constantes pour divers points des courbes de titrage. Nous avons obtenu ainsi les valeurs suivantes que nous adopterons par la suite:

$$\mathrm{p}K_1^{\mathrm{H}} = 11.59 \pm 0.03 \text{ (moyenne de 32 valeurs)}$$

$$\mathrm{p}K_2^{\mathrm{H}} = 2.39 \pm 0.02 \text{ (moyenne de 48 valeurs)}$$

DÉTERMINATION DES CONSTANTES DE STABILITÉ

La neutralisation par la soude de solutions contenant l'ion métallique et le coordinat à différents rapports *R* (Tableau I) en présence d'acide nitrique permet de tracer la courbe de formation $\bar{n} = \mathrm{f}(\mathrm{p}[\mathrm{ASS}])$ où $\bar{n}$ représente le nombre moyen de coordinats liés au métal.

TABLEAU I

RAPPORTS DE L'ION MÉTALLIQUE ET DE L'ACIDE SULFO-5-SALICYLIQUE

$R = [ASS]_T/[Fe]_T$	$[Fe(III)]_T$	$[ASS]_T$	$[HNO_3]_T$
10	$1.032 \cdot 10^{-3}$	$9.925 \cdot 10^{-3}$	$9.96 \cdot 10^{-3}$
15	$1.032 \cdot 10^{-3}$	$1.489 \cdot 10^{-2}$	$9.96 \cdot 10^{-3}$
20	$1.032 \cdot 10^{-3}$	$2.002 \cdot 10^{-2}$	$9.96 \cdot 10^{-3}$
30	$1.032 \cdot 10^{-3}$	$3.003 \cdot 10^{-2}$	$9.96 \cdot 10^{-3}$

Nous avons en effet calculé $\bar{n}$ et [ASS], nécessaires au tracé de ces courbes à l'aide d'un ordinateur Bull GE 235 en fournissant comme données les concentrations initiales des différents constituants, les constantes d'ionisation du coordinat, le volume de soude ajouté et le potentiel correspondant de l'électrode en verre.

Dans le but d'éviter une hydrolyse de l'ion ferrique nous avons choisi des valeurs élevées de *R*.

Les différents rapports examinés (Tableau I) conduisent à une courbe de formation unique (Fig. 1) ce qui exclut l'hypothèse de la présence d'espèces protonées, hydroxydées ou polynucléaires aux valeurs extrêmes de log [ASS].

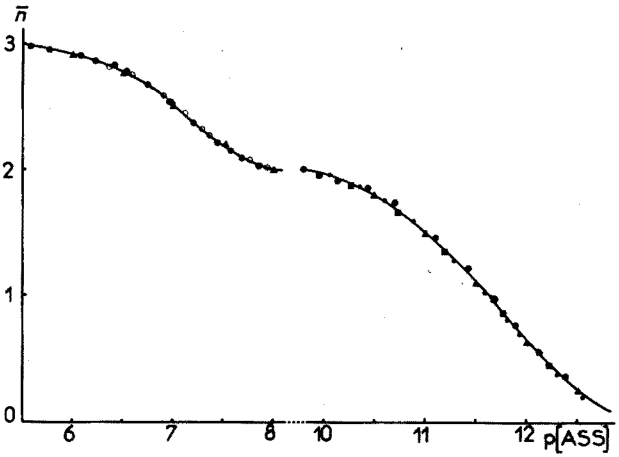

Fig. 1. Courbe de formation du système Fe(III)–acide sulfo-5-salicylique. (■) Rapport 10, (*) rapport 15, (●) rapport 20, (○) rapport 30, (▲) points recalculés.

On peut alors en appliquant la méthode des moindres carrés aux données $\bar{n}$ et [ASS] obtenir des valeurs affinées des constantes de stabilité tenant compte de l'ensemble des points de la courbe de formation. C'est ainsi que l'on obtient les valeurs ci-dessous qui sont constantes après 4 itérations successives (ordinateur IBM 1620).

$\log K_1 = 12.08$	$\log \beta_1 = 12.08$
$\log K_2 = 11.14$	$\log \beta_2 = 23.22$
$\log K_3 = 7.02$	$\log \beta_3 = 30.24$

En possession de ces données nous avons calculé les concentrations de toutes les espèces présentes simultanément en solution en fonction du pH pour les conditions utilisées ci-dessous lors de l'étude par la méthode trichrome. Nous avons donc tracé sur les Fig. 2,3 et 4, les courbes représentant les concentrations des espèces $[\mathrm{Fe(ASS)}_n]$ en fonction du pH.

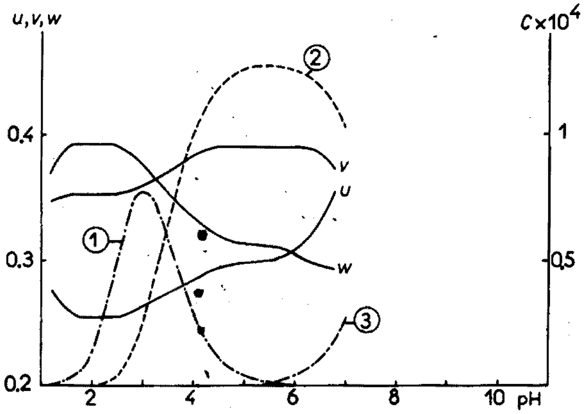

Fig. 2. Méthode trichrome (traits pleins) et courbes de répartition (traits discontinus) pour le rapport 10. ① [FeASS]; ② $[\mathrm{Fe(ASS)_2}]$; ③ $[\mathrm{Fe(ASS)_3}]$.

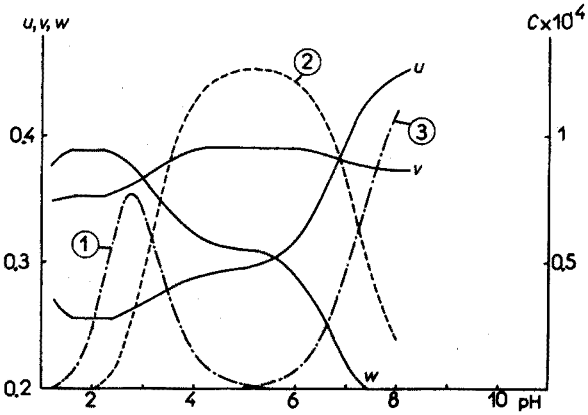

Fig. 3. Méthode trichrome (traits pleins) et courbes de répartition (traits discontinus) pour le rapport 20. ① [FeASS]; ② $[\mathrm{Fe(ASS)_2}]$; ③ $[\mathrm{Fe(ASS)_3}]$.

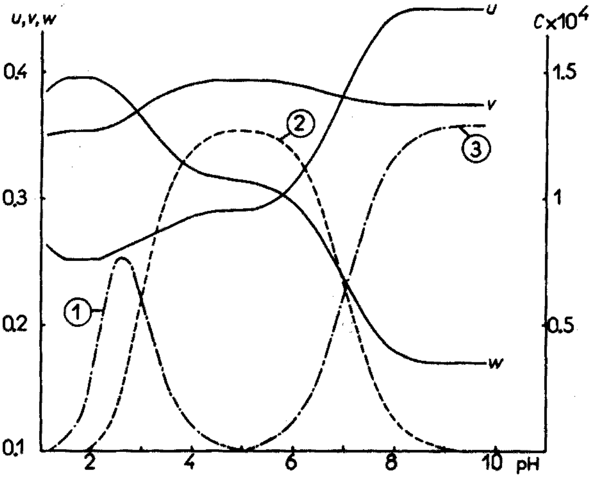

Fig. 4. Méthode trichrome (traits pleins) et courbes de répartition (traits discontinus) pour le rapport 30. ① [FeASS]; ② [Fe(ASS)$_2$]; ③ [Fe(ASS)$_3$].

MÉTHODE TRICHROME

Nous ne développerons pas le principe de la méthode trichrome mise au point en 1960 par Reilley et ses collaborateurs[10,11]. Quelques publications ont montré la valeur de cette méthode d'investigation des équilibres en solution, notamment en ce qui concerne les complexes mixtes bimétalliques par Flaschka[12], et dans notre Laboratoire par Petit-Ramel et Pâris[13].

Après avoir tracé les spectres d'absorption en fonction du pH, trois intervalles spectrophotométriques (385–435, 435–485 et 485–535 nm) sont utilisés pour étudier la partie choisie de la courbe d'absorption, et plusieurs longueurs d'ondes (10 dans notre étude) sont repérées dans chaque intervalle. La somme de toutes les absorptions pour chaque longueur d'onde sera caractérisée par une fonction $U = \sum_{i=1}^{10} A_{1i}$ dans le premier intervalle, $V = \sum_{i=1}^{10} A_{2i}$ dans le second et $W = \sum_{i=1}^{10} A_{3i}$ dans le troisième.

On peut alors introduire trois nouvelles fonctions:

$$u = U/(U+V+W) \quad v = V/(U+V+W) \quad w = W/(U+V+W)$$

où bien entendu u, v, w sont alors indépendants de la concentration de la substance colorée puisque U, V, W sont proportionnels à cette concentration.

Il est alors possible d'étudier l'évolution d'un équilibre en fonction du pH. En effet les graphes $u = \mathrm{f(pH)}$ par exemple, ainsi obtenus doivent présenter des paliers parallèles à l'axe des pH, si ce facteur n'affecte pas l'équilibre. De tels paliers seront obtenus dans chaque domaine de pH où un complexe unique est formé progressivement puisque la valeur de u est indépendante de la concentration. Ainsi, par exemple, le graphe $u = \mathrm{f(pH)}$ révèlera les domaines d'existence en fonction du pH de chaque complexe du système étudié. Les portions non parallèles à l'axe des pH de tels graphes indiquent les domaines de transition entre deux complexes successifs.

Nous avons effectué des essais pour trois rapports différents de réactifs engagés.

$R = [\mathrm{ASS}]_T/[\mathrm{Fe(III)}]_T = 10$; $[\mathrm{Fe(III)}]_T = 1.290 \cdot 10^{-4}$ $[\mathrm{ASS}]_T = 1.250 \cdot 10^{-3}$
$R = 20$; $[\mathrm{Fe(III)}]_T = 1.290 \cdot 10^{-4}$ $[\mathrm{ASS}]_T = 2.500 \cdot 10^{-3}$
$R = 30$; $[\mathrm{Fe(III)}]_T = 1.290 \cdot 10^{-4}$ $[\mathrm{ASS}]_T = 3.750 \cdot 10^{-3}$

Dans les trois cas on observe de façon très nette le palier correspondant à la formation du premier complexe [FeASS] (coloration violette intense) pour des pH compris environ entre 1.50 et 2.50 (Fig. 2, 3 et 4). Les courbes de répartition montrent qu'au delà de cette valeur l'espèce $[\mathrm{Fe(ASS)_2}]$ existe de façon notable, on a donc équilibre entre deux espèces colorées distinctes, ce qui explique que le premier palier des courbes *u*, *v*, *w* soit limité à cette valeur.

De même pour les trois rapports le palier correspondant à la formation du deuxième complexe $[\mathrm{Fe(ASS)_2}]$ (coloration rouge orangée) est peu marqué. Ici encore les courbes de répartition expliquent ce fait puisque l'on voit que cette espèce n'existe pratiquement jamais seule en solution mais qu'elle est en équilibre soit avec le premier complexe ($\mathrm{pH} < 5$) soit avec le troisième ($\mathrm{pH} > 5$). Enfin il faut remarquer que l'on observe le palier correspondant à la formation du troisième complexe $[\mathrm{Fe(ASS)_3}]$ (coloration jaune) uniquement pour le rapport 30 et pour des pH supérieurs à 8.50 en accord avec la courbe de répartition qui montre qu'à partir de cette valeur la concentration en $[\mathrm{Fe(ASS)_2}]$ devient négligeable et qu'une seule espèce colorée subsiste au sein de la solution.

Nos résultats potentiométriques sont donc corroborés parfaitement par cette étude spectrophotométrique trichromatique.

CONCLUSION

Dans le cas des cations métalliques trivalents présentant la plupart du temps des phénomènes complexes d'hydrolyse qui viennent se superposer au processus de chélation, le calcul des constantes de stabilité des complexes formés est souvent difficile. En employant des rapport élevés coordinat/cation métallique, nous avons pu éviter cet inconvénient.

Des mesures précises de pH associées à la méthode d'exploitation de Bjerrum nous ont conduits aux valeurs des constantes de stabilité des complexes $[\mathrm{Fe(ASS)}_n]$ ($n = 1$, 2 et 3) existant à l'exclusion de toute autre espèce dans le système Fe(III)–acide sulfo-5-salicylique, le troisième complexe n'apparaissant d'ailleurs de façon notable que lorsque la concentration de l'agent chélatant est de vingt fois supérieure à celle de l'ion ferrique.

Les valeurs obtenues ont été affinées par la méthode des moindres carrés. Nous avons pu alors calculer la répartition des diverses espèces chélatées en fonction du pH. Cette répartition a été confirmée sans ambiguité par la spectrophotométrie trichrome mettant en évidence la formation successive et les domaines d'existence des trois complexes.

Enfin à l'inverse des cas du Tiron et de l'acide amino-4-salicylique nous montrons qu'il n'y a pas formation d'espèces protonées et ce résultat est en accord avec un travail récent sur les salicylates ferriques[14].

RÉSUMÉ

Les auteurs étudient, au moyen de méthodes potentiométrique et spectrophotométrique, la complexation des ions ferriques avec l'acide sulfo-5-salicylique. Les domaines d'existence, les compositions et les constantes de stabilité des espèces formées sont données.

SUMMARY

The complex formation of iron(III) with sulfosalicylic acid has been studied by potentiometric and spectrophotometric measurements. The ranges of formation, the composition and the stability constants of the species formed are described.

ZUSAMMENFASSUNG

Die Komplexbildung zwischen Eisen(III) Ionen und Sulphosalicylic Säure wurde durch potentiometrische Messungen untersucht. Die Stabilitätskonstanten und das Bildungsgebiet der Komplexen wurden berechnet, und die Resultaten durch trichromatische Spektrophotometrie geprüft.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

TRANSIENT PHENOMENA OF ION-SELECTIVE MEMBRANE ELECTRODES

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(Received 15th May 1971)

The potential of ion-selective membrane electrodes is a result of ion-exchange equilibria established on the membrane surfaces[1]. The rate of the exchange reaction greatly influences the behaviour of the electrodes: if the rate of the exchange reaction is too low, then the electrode is not reversible to the appropriate ion. Accordingly, it is very important to study the kinetics of the exchange reactions; it is possible to do this by measuring the response time of the electrodes, which is, of course, also extremely significant from a practical point of view. More and more ion-selective electrodes have already been used in flowing systems and the application of ion-selective electrodes in controlling systems as sensors can also be foreseen.

Only a few papers have so far appeared in the literature on the transient phenomena of ion-selective electrodes including glass electrodes[2-13], and the results published have not been entirely satisfactory. The research discussed below concerned the examination of ion-selective electrodes based on slightly soluble precipitates. Suitable measuring units and methods have been worked out and the response time of the halide, cyanide and sulphide ion-selective electrodes were determined.

EXPERIMENTAL

Electrode system

For the measurements ion-selective electrodes (Types OP-Cl-711, OP-Br-711, OP-I-711 and OP-CN-711, Radelkis, Budapest, Hungary) and a standard calomel reference electrode (Shott and Gen) were used. Before measurements the ion-selective electrodes were pretreated in a 10^{-3} *M* solution of the appropriate anion for 2 h and then washed with distilled water.

In the measuring cell constructed, an interchange of two different concentrations of the appropriate ion round the electrode within 1 millisecond was ensured, and a solution layer provided contact between the ion-selective and the reference electrode.

E.m.f. measurements

All measurements were carried out at 25° with a d.c. amplifier (Diodenverstärker Type 71s, Knick, Berlin 37, Germany) which had an input impedance of 10^{12} Ω in combination with an RTF oscilloscope (VEB Funkwerk, Köpenick). The time constant of the unit, including the measuring cell, was 2 msec.

Reagents

Chemicals used were of pro analysi grade.

RESULTS AND DISCUSSION

A variation of the immersion method was used for measuring the response time of the ion-selective electrodes *i.e.* the time taken for the electrode potential to attain a constant value. Two different concentrations (10^{-2} and 10^{-3} M) of the appropriate ion were interchanged round the electrode. As the e.m.f. *versus* time curve of the iodide electrode shows, the electrode potential reached a constant value within a few hundred milliseconds, when potassium iodide solutions were used (Fig. 1).

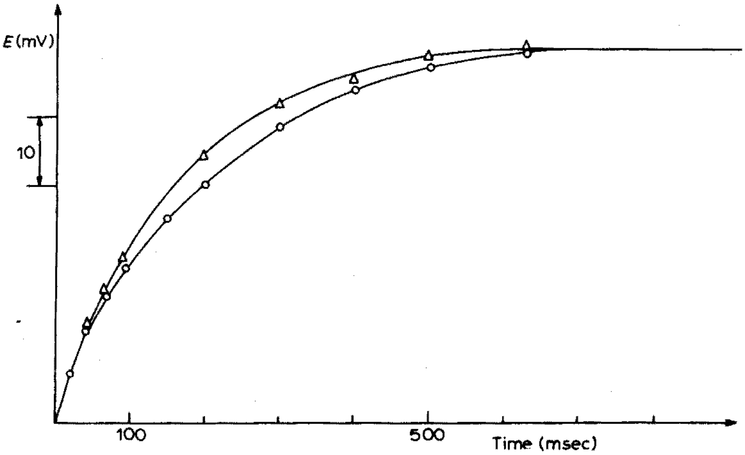

Fig. 1. E.m.f. *versus* time curve for the iodide ion-selective electrode. The concentration of the iodide solution was changed from 10^{-2} M to 10^{-3} M. (○——○) calculated, (△——△) measured.

On the basis of the results the following kinetic equation could be derived for describing the e.m.f. *versus* time function:

$$E = E_{t=0} + k_1(1 - e^{k_2 t}) \quad (1)$$

where $E_{t=0}$ is the potential established at zero time, k_1 and k_2 are constants, and t is the time.

The curves of e.m.f. *versus* time for the chloride, bromide, and cyanide ion-selective electrodes were similar to that of the iodide electrodes, which means that the response time of these electrodes can also be described with one exponential equation.

Of the detailed experimental results only those which were obtained with the iodide ion-selective electrodes will be discussed. The response time of the electrode was measured as a function of the following parameters.

Thickness of the membrane layer. For these experiments, the electrodes used had membrane layers which varied in thickness (0.9, 1.5 and 2 mm). The results showed that the response time of the electrodes is independent of the thickness of the membrane layer in the range examined (Fig. 2).

This experiment is very important with respect to the application of the ion-

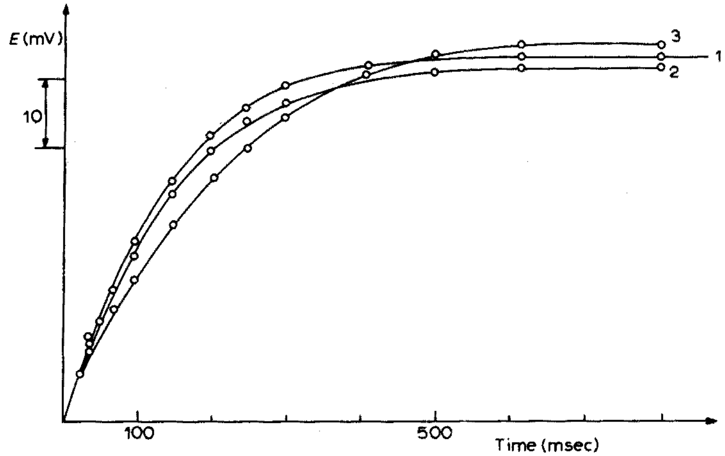

Fig. 2. E.m.f. *versus* time curve for the iodide ion-selective electrode as a function of the membrane thickness. The concentration of the iodide solution was changed from 10^{-2} *M* to 10^{-3} *M*. (1) 0.9 mm; (2) 1.5 mm; (3) 2.0 mm.

selective electrodes in industry, where the use of electrodes having a thicker membrane layer is favourable.

Direction of the concentration jump. On the basis of the experimental results, it can be stated that the response time of the electrode depends on the direction of the concentration jump (Fig. 3). The response is faster when the solution surrounding the electrode becomes stronger, compared with the response to progressively weaker solutions.

Effect of other ions. Large amounts of other ions (chloride or bromide) generally decrease the response time. The iodide concentrations of the solutions were 10^{-2} *M* and 10^{-3} *M*, while the concentration of the other ion, *e.g.* chloride, was varied in the range of 10^{-1} and 10^{-4} *M* concentration (Fig. 4). The response time of an iodide electrode in the presence of other ions was found to be smaller than in the absence of these ions, which may be the result of a faster dehydration of the iodide ion. Further experiments along these lines are in progress.

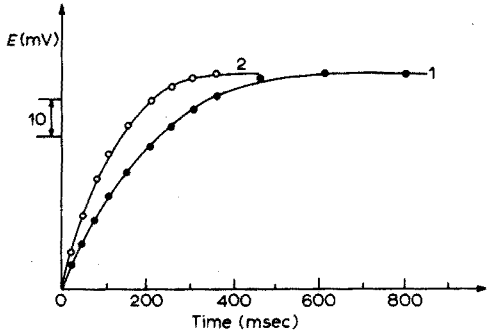

Fig. 3. Effect of the direction of concentration jump on the e.m.f. *versus* time curve for the iodide ion-selective electrode. (1) 10^{-2} *M*–10^{-3} *M* KI; (2) 10^{-3} *M*–10^{-2} *M* KI.

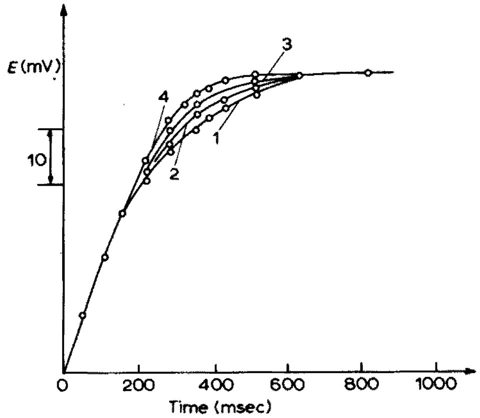

Fig. 4. E.m.f. *versus* time curve for the iodide ion-selective electrode in the presence of various concentrations of chloride. (1) 10^{-2} *M*–10^{-3} *M* KI; (2) 10^{-2} *M*–10^{-3} *M* KI in the presence of 10^{-3} *M* KCl; (3) 10^{-2} *M*–10^{-3} *M* KI in the presence of 10^{-2} *M* KCl; (4) 10^{-2} *M*–10^{-3} *M* KI in the presence of 10^{-1} *M* KCl.

The response time of the cyanide electrode is similar to that of a halide electrode, which also shows that the mechanism of the response is the same.

SUMMARY

A method of studying the response time of the ion-selective electrodes has been worked out. An exponential equation has been derived to describe the response of the electrodes. The potential of the silver halide electrodes reaches a constant value within a few hundred milliseconds, from which it follows that these electrodes can be used advantageously as sensors in flowing and control systems.

RÉSUMÉ

Une méthode est mise au point pour examiner le temps de réponse des électrodes ion-sélectives, proposant une équation exponentielle. Le potentiel de l'électrode à halogénure d'argent atteint une valeur constante dans l'espace de quelques cent millisecondes. Ces électrodes peuvent par conséquent être avantageusement utilisées comme détecteurs pour des contrôles et des systèmes en mouvement.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Untersuchung der Ansprechzeit ionenselektiver Elektroden entwickelt. Für die Beschreibung des Elektrodenverhaltens wurde eine Exponentialgleichung abgeleitet. Das Potential von Silberhalogenidelektroden erreicht innerhalb weniger Hundert Millisekunden einen konstanten Wert, woraus folgt, dass diese Elektroden vorteilhaft als Sensoren bei Fliessystemen und Steuereinrichtungen verwendet werden können.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ADSORPTION OF GUANINE AND GUANOSINE AT THE PYROLYTIC GRAPHITE ELECTRODE

IMPLICATIONS FOR THE DETERMINATION OF GUANINE IN THE PRESENCE OF GUANOSINE

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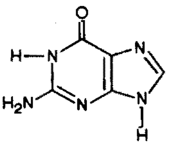
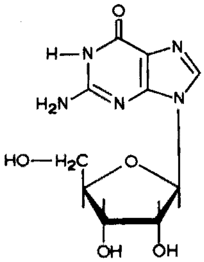
(Received 7th June 1971)

Recently, the mechanism of electrochemical oxidation of guanine (I) at the pyrolytic graphite electrode in aqueous solution was reported[1]. The electrochemical oxidation of guanosine (II) is currently under study.



(I)



(II)

The mechanism of electrooxidation of guanosine appears to be somewhat different from that of guanine and will be reported elsewhere. However, particularly significant from an analytical viewpoint is the fact that the voltammetric oxidation peak potentials for guanine and guanosine are quite different. This suggested that it would be worthwhile studying the analytical utility of this effect, in particular for determining guanine in the presence of guanosine.

The ultraviolet absorption spectra of guanine and guanosine are very similar so that it is very difficult to obtain a simple analysis for such mixtures. Generally, when analyses of such mixtures are required, the base and its nucleoside are separated by paper or thin-layer chromatography[2,3] and then the individual compounds are determined separately. Udenfriend and Zaltzman[4] indicated that guanine and guanosine have slightly different fluorescent spectra so that it might be possible to determine mixtures of the two compounds. Other methods for the analysis of guanine have been briefly reviewed elsewhere[4-6]. None of the methods previously reported are capable of determining very low concentrations of guanine in the presence of large amounts of guanosine.

The work reported here outlines several approaches to characterize adsorption of guanine and guanosine at the pyrolytic graphite electrode, the effects of guanosine on the extent of adsorption of guanine and, based on the foregoing information, methods for the determination of guanine in the presence of guanosine.

EXPERIMENTAL

Chemicals

Guanine and guanosine were obtained from Nutritional Biochemicals. Buffer solutions were prepared from reagent grade chemicals and, with the exception of 1 *M* acetic acid, had an ionic strength of 0.5 *M*.

Apparatus

D.c. voltammograms were obtained with the apparatus described by Dryhurst, Rosen and Elving[7]. A.c. voltammograms were obtained with an operational amplifier instrument combined with a Princeton Applied Research Model 121 Lock-in Amplifier/Phase Detector. For a.c. voltammetry a d.c. ramp of 5 mV sec^{-1} and a sinusoidal signal of 100 Hz and 10 mV peak-to-peak was employed for all experiments. All voltammograms were recorded on Hewlett-Packard Model 7001A X-Y recorders. A three-compartment cell maintained at 25 ± 0.1° was employed containing a saturated calomel reference electrode (S.C.E.) and a platinum gauze counterelectrode. All potentials are referred to the S.C.E. at 25°.

Preparation of pyrolytic graphite electrode

The pyrolytic graphite employed in this study was obtained from Super-Temp Company (Santa Fe Springs, Calif.). Small rods of 4 mm diameter and 1 cm length were machined and were sealed into a 4-mm i.d. glass tube with Hysol Epoxi-Patch (Hysol Corporation, Olean, N.Y.). The electrode was ground flush with the end of the glass tube.

Voltammetric procedure

For d.c. voltammetry the pyrolytic graphite electrode was resurfaced before every voltammogram was run by polishing on a 600-grade silicon carbide paper mounted on a metallographic polishing wheel (Buehler Inc., Evanston, Ill.). The surface of the electrode was then washed for about 10–15 sec with a fine spray of water. The shaft of the electrode was then dried thoroughly; any excess water remaining on the electrode surface was removed by touching the surface very gently with a soft absorbent paper tissue.

Test solutions were not deaerated. The pyrolytic graphite electrode was inserted into the test solution and after 10 sec at the initial potential (always 0.4 V for d.c. voltammetry) the voltage scan was commenced. At least three replicate voltammograms were recorded at each concentration.

For a.c. voltammetry a slightly modified procedure was employed in order to obtain reproducible data. It was found even in pure background solution that after each resurfacing of the graphite electrode the alternating base current was rather variable. This is undoubtedly due to considerable changes in the double-layer capacity owing to variations in surface roughness. Thus, after resurfacing the electrode one set of data was obtained by immersing the electrode in the appropriate background solution and applying the initial potential (0.00 V) for 10 sec; the voltammetric scan was then commenced. At the end of the scan, the electrode was removed from the cell and the shaft carefully dried, but without allowing the electrode surface to become dry. After 30 sec the electrode was replaced in the cell and another background trace was recorded. This procedure was always carried out three times. Under these conditions the background traces always agreed very closely (*vide infra*).

After completion of the last background trace the electrode was removed and treated exactly as just described, but the background solution in the cell was replaced by the test solution in the same background. After 30 sec the electrode was replaced and the sample trace was recorded at least twice.

For every solution examined this procedure was repeated at least three times. Although the voltammograms recorded on identical background and test solutions in this manner were not reproducible after the electrode had been resurfaced, the qualitative shape of the traces, *i.e.*, regions of base current depressions and elevations, were identical.

Procedure for determination of guanine in the presence of guanosine

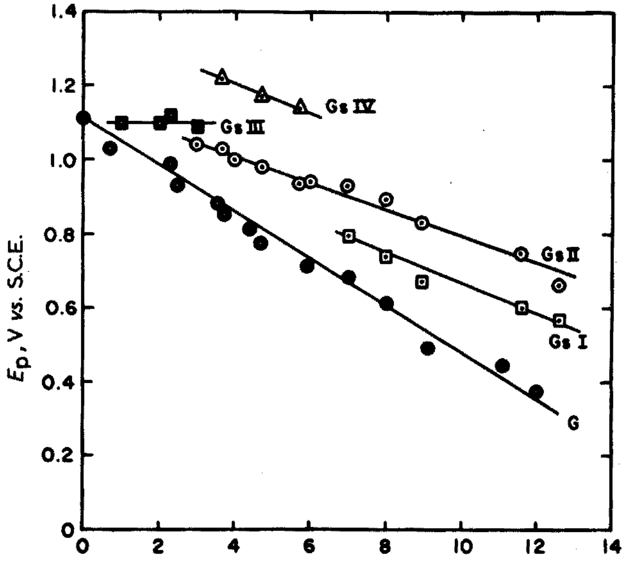
The guanine sample, which may or may not contain any guanosine, is weighed into a 25-ml volumetric flask and dissolved in 1 *M* acetic acid or McIlvaine buffer pH 4 or 7. Then, 0.0185–0.0195 g of guanosine are added. (This is sufficient to make the solution *ca.* 2.5 m*M* with respect to guanosine.) The resultant solution is then diluted to 25.00 ml and set aside with frequent shaking for about 2 h. In 1 *M* acetic acid the guanosine readily dissolves; in the McIlvaine buffers the guanosine is not completely soluble. A voltammetric trace starting from 0.4 V is then run at a clean resurfaced pyrolytic graphite electrode with a voltage scan rate of 5 mV $\sec^{-1}$. At least three voltammograms should be recorded. A background voltammogram is recorded in exactly the same way except that the guanine sample is omitted. The mean background current at the guanine peak potential is subtracted from the mean guanine peak current. The concentration of guanine is then determined from a calibration curve prepared for known guanine concentrations (between 0.04 and 0.5 m*M*) in the presence of excess guanosine (*i.e.*, 0.0185–0.0195 g of guanosine per 25 ml of solution) in the appropriate supporting electrolyte.

RESULTS AND DISCUSSION

Linear sweep voltammetry

A preliminary examination of the voltammetric peak potentials of guanine and guanosine over the normal pH range showed that guanine gives a single oxidation peak between pH 0 and 13 which occurs at more positive potentials than any of the four oxidation peaks of guanosine at all pH values (Fig. 1). Although the appearance of four guanosine peaks would appear to be very complex, in fact only peak III below pH 3 and peak II between pH 3 and 13 are well formed. Peak I is a rather ill-defined pre-peak that is observed on the rising portion of peak II, and peak IV is a very small post-peak. The latter two peaks are only observed clearly at low scan rates and are undoubtedly associated with the adsorption of guanosine and possibly its oxidation products at the pyrolytic graphite electrode.

Three buffer systems were selected for examination of the analytical relationship of the peak current to the concentration of guanine and guanosine in pure solu-



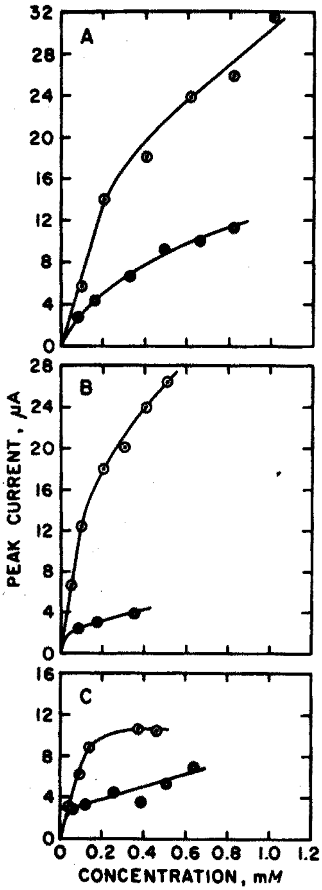


Fig. 1. Variation of E_p with pH for the single voltammetric oxidation peak of guanine (G) and for the four voltammetric oxidation peaks of guanosine (Gs). Guanine concentration, 0.300 mM; guanosine concentration, 0.302 mM; scan rate, 5 mV sec^{-1}; pyrolytic graphite electrode geometric area, 12.5 mm^2.

Fig. 2. Variation of peak current with concentration for the voltammetric oxidation of guanine (–○–) and guanosine (–●–) at the pyrolytic graphite electrode in (A) 1 M acetic acid, pH 2.3 (guanosine peak III); (B) McIlvaine pH 4 (guanosine peak II); and (C) McIlvaine pH 7 (sum of guanosine peaks I and II). Scan rate, 5 mV sec^{-1}; pyrolytic graphite electrode geometric area, 12.5 mm^2.

tions, namely 1 M acetic acid (pH 2.3), and McIlvaine buffers pH 4 and 7. Typical data are presented graphically in Fig. 2. In each of the background electrolyte systems employed, there is a non-linear relationship between the peak current and concentration for guanine and guanosine. Guanine is more soluble in 1 M acetic acid than in the McIlvaine buffers pH 4 and 7, which allows a rather more extensive concentration range to be studied. In the latter two buffer systems the maximum solubility of guanine is *ca.* 0.5 mM. Guanosine is initially soluble to greater than 1–2 mM in all the buffer systems employed, but even at the 1 mM level it partially precipitates after standing for about 12 h.

In the case of both guanine and guanosine the peak potentials shift appreciably to more positive potential with increasing concentration. Over the approximate concentration range of 0.05–0.5 m*M* this shift is of the order of 70–100 mV for both compounds. In the case of guanine in McIlvaine buffer pH 4 the shift of peak potential means that no distinguishable peak is observed at concentrations above *ca.* 0.35 m*M* (Fig. 2).

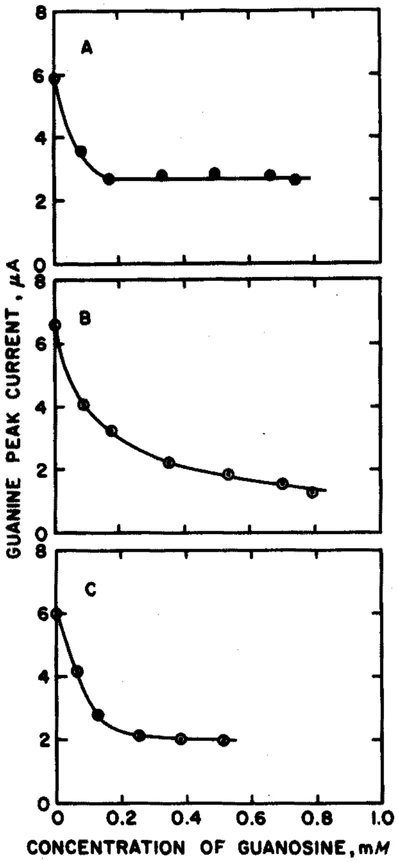
In McIlvaine buffer pH 7 guanine shows one and occasionally two post-peaks at more positive potentials than the main peak. These peaks occur at rather variable potentials. In almost saturated solutions of McIlvaine pH 7 the post-peaks are very pronounced (*vide infra*). Such behavior is typical of an electrode reaction where the reactant is strongly adsorbed.

Nevertheless, the i_p *vs.* C curves shown in Fig. 1 appeared to be sufficiently definitive and reproducible to allow guanine to be determined in the presence of guanosine. However, when mixtures of guanine and guanosine were examined, it became obvious that the presence of guanosine caused a most pronounced depression of the peak current for guanine. In order to illustrate this effect a fixed concentration of guanine was taken and increasing amounts of guanosine were added. Typical data are presented in Fig. 3. The data presented in Figs. 2 and 3 appear to support the view that both guanine and guanosine are adsorbed at the pyrolytic graphite electrode. However, in view of the fact that guanosine depresses the guanine peak current even at relatively low guanosine concentrations, it is likely that in mixtures of the two compounds a competitive adsorption takes place with guanosine displacing some adsorbed guanine from the electrode surface.

In order to define better the adsorption processes occurring at the electrode, the effect of voltage scan rate on the peak voltammograms of guanine, guanosine and mixtures of the two were examined. The theoretical equation for a linear diffusion-controlled irreversible peak voltammogram[8] at a plane electrode is:

$$(i_p)_{\mathrm{irrev}} = 2.98 \times 10^5 n(\alpha n_a)^{\frac{1}{2}} A D^{\frac{1}{2}} v^{\frac{1}{2}} C \qquad (1)$$

where $(i_p)_{\mathrm{irrev}}$ is the peak current in μA, n the total electron number, α the electron transfer coefficient, n_a the number of electrons involved in the rate-controlling electron-transfer process, A the electrode area (cm^2), D the diffusion coefficient of the electroactive species (cm^2 sec^{-1}), v the voltage scan rate (V sec^{-1}) and C the bulk concentration of the electroactive species (m*M*). According to this equation $i_p/ACv^{\frac{1}{2}}$, the peak current function, should be a constant, so that a plot of this function *versus* $v^{\frac{1}{2}}$ should be a straight line parallel to the $v^{\frac{1}{2}}$ axis. However, in the case of guanine and guanosine (Fig. 4), the peak current function shows a distinct increase with increasing scan rate. This behavior is typical of an electrode process where the reactant is adsorbed at the electrode surface. This is so because the adsorbed material constitutes a fixed amount of material and hence charge flow, while the amount of material diffusing to the electrode surface is time-dependent. As the scan rate increases, the contribution of diffusing material decreases with respect to the amount of adsorbed material reacting at the electrode surface. Accordingly, an increase in scan rate causes the peak current function to increase[9]. The data presented in Fig. 3 suggested that a 5–10-fold excess of guanosine depressed the peak current of guanine to a minimum and more or less constant value. Thus for illustrative purposes, data are presented in Fig. 4 for the peak current function of guanine in 1 *M* acetic acid, McIlvaine pH 4 and McIlvaine pH 7 in the presence of 9-, 15- and 6-fold excesses of guanosine, respectively. It is clear that under all these conditions the peak current function of guanine exhibits



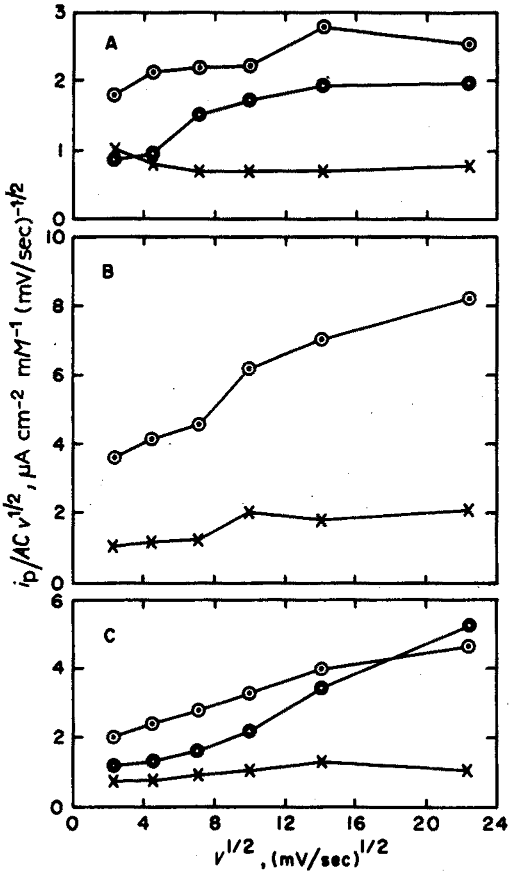


Fig. 3. Effect of guanosine on the peak current of guanine. (A) 0.1023 m*M* guanine in 1 *M* acetic acid pH 2.3; (B) 0.0509 m*M* guanine in McIlvaine buffer pH 4; (C) 0.0917 m*M* guanine in McIlvaine buffer pH 7.

Fig. 4. Variation of peak current function, $i_p/ACv^{\frac{1}{2}}$, with the square root of voltage scan rate for guanine (–○–), guanosine (–●–) and guanine in the presence of excess guanosine (– x –). (A) 1 *M* acetic acid background: 0.1023 m*M* guanine; 0.1644 m*M* guanosine; 0.1023 m*M* guanine plus 0.921 m*M* guanosine. (B) McIlvaine pH 4 background: 0.0509 m*M* guanine; 0.0509 m*M* guanine plus 0.8032 m*M* guanosine. (C) McIlvaine pH 7 background: 0.0821 m*M* guanine; 0.0649 m*M* guanosine; 0.0821 m*M* guanine plus 0.520 m*M* guanosine. Pyrolytic graphite electrode geometric area, 12.5 mm^2.

behavior close to that expected for a diffusion-controlled electrode reaction. It appears therefore that, in the presence of large amounts of guanosine, guanine is displaced from the electrode surface and the oxidation becomes essentially diffusion-controlled.

A.c. voltammetry

A.c. polarography is an excellent qualitative technique for observing adsorption of organic molecules at a dropping mercury electrode. Over the potential regions where adsorption occurs, pronounced depressions of the alternating base current occur, owing to a decrease of the double-layer capacity of the electrode[10]. Few reports

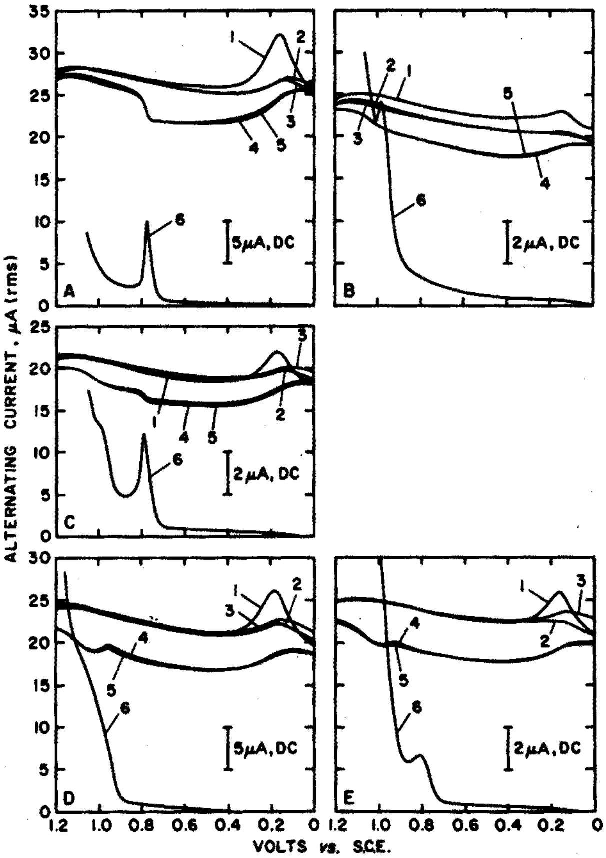


Fig. 5. A.c. voltammograms at the pyrolytic graphite electrode in McIlvaine buffer pH 4 of (A) 0.055 m*M* guanine; (B) 0.107 m*M* guanosine; (C) 0.055 m*M* guanine plus 0.107 m*M* guanosine; (D) 0.85 m*M* guanosine; (E) 0.055 m*M* guanine plus 0.85 m*M* guanosine. Scan rate, 5 mV sec^{-1}; alternating voltage, 10 mV peak-to-peak; 100 Hz; pyrolytic graphite electrode, 12.5 mm^2. Scans 1, 2, 3 are a.c. background traces. scans 4 and 5 are a.c. traces in the presence of guanine, guanosine or both, scan 6 is a d.c. voltammogram.

of a.c. techniques at solid electrodes have appeared[11-15] although the use of such techniques for the study of adsorption at stationary mercury electrodes has been reported[16].

A.c. voltammograms of guanine, guanosine and mixtures of the two at the pyrolytic graphite electrode in McIlvaine buffers pH 4 and 7 are presented in Figs. 5 and 6. Although not of interest with respect to this study, it was noticed that the first a.c. voltammogram at a freshly resurfaced electrode in background solutions always exhibited a distinct peak at *ca.* 0.15 V in McIlvaine pH 4 and at *ca.* 0.025 V in McIlvaine pH 7 buffer; this may be due to a surface oxidation effect or to reduction of a surface oxide. After the first a.c. sweep the subsequent voltammograms showed little evidence of the latter peak.

It is clear from the data in Figs. 5 and 6 that, for each set of data for runs A–E, the background and sample a.c. voltammograms are quite reproducible. However, after the electrode has been resurfaced, even the background voltammograms show a

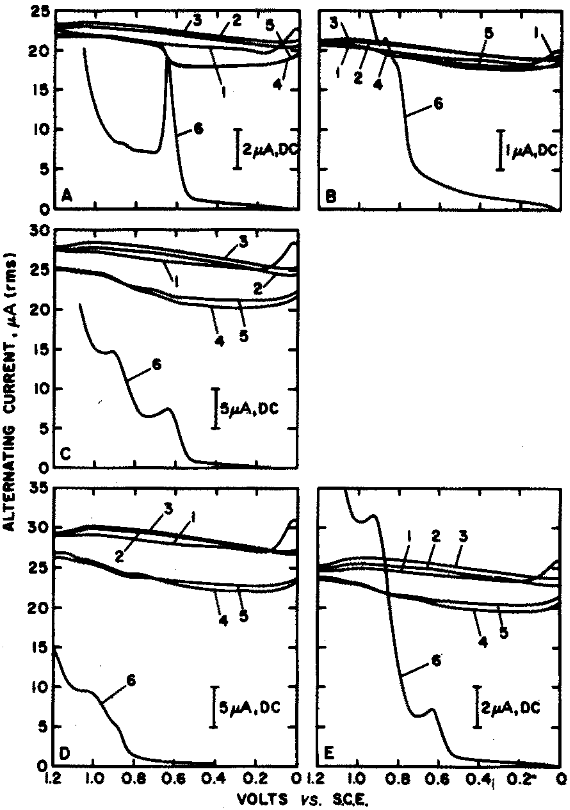


Fig. 6. A.c. voltammograms at the pyrolytic graphite electrode in McIlvaine buffer pH 7 of (A) 0.080 m*M* guanine; (B) 0.080 m*M* guanosine; (C) 0.080 m*M* guanine plus 0.15 m*M* guanosine; (D) 0.65 m*M* guanosine; (E) 0.08 m*M* guanine plus 0.65 m*M* guanosine. Scan rates etc. and scans 1–6 as in Fig. 5.

variability of 10–15%. The current observed for a.c. voltammograms is much larger than would be observed for a stationary mercury electrode having the same geometric surface area as the pyrolytic graphite electrode. This undoubtedly reflects the surface roughness of the graphite electrode which is expected to result in a large alternating base or charging current.

Nevertheless, in spite of these limitations of a.c. voltammetry at the pyrolytic graphite electrode, the qualitative form of the voltammograms is most revealing. Considering data for McIlvaine buffer pH 4, it is clear that for guanine (Fig. 5A) a pronounced base current depression occurs at potentials negative of the d.c. voltammetric peak, and this depression essentially disappears at potentials positive of the d.c. peak. This is typical of an electrode reaction where the reactant is adsorbed but the product(s) is not. A very characteristic and sharp increase in the base current coincides with the d.c. peak potential. The fact that no a.c. peak is observed confirms the irreversibility of the electrode reaction[1]. Guanosine (Fig. 5B) also clearly depresses the base current, but a characteristic and sharp change in the base current is not observed at potentials near the d.c. peak. This may indicate that both guanosine and one of its oxidation products are adsorbed at the pyrolytic graphite electrode. The effect of a two-fold excess of guanosine on the a.c. voltammogram of guanine (Fig. 5C) shows that the characteristic increase of the base current of guanine at its d.c. peak potential is considerably reduced. Coupled with the earlier observation that the d.c. peak current of guanine is also depressed in the presence of guanosine, this confirms that guanosine displaces adsorbed guanine from the electrode surface. That this is so is even more apparent in Fig. 5D and E which show the a.c. voltammogram of 0.85 m*M* guanosine (Fig. 5D) and 0.055 m*M* guanine in the presence of 0.85 m*M* guanosine (Fig. 5E). In the latter case no base current elevation near the guanine d.c. peak is observed, which suggests that in the presence of such a large excess of guanosine, guanine is not appreciably adsorbed. The earlier scan rate studies (Fig. 4) qualitatively confirm this conclusion.

Almost exactly the same interpretation can be applied to the a.c. voltammograms observed in McIlvaine buffer pH 7 (Fig. 6 A–E).

At high concentrations of guanine in McIlvaine buffer, one or two large post-peaks were observed by d.c. voltammetry. Comparison of the a.c. voltammograms of 0.4 m*M* guanine in McIlvaine buffer pH 7 with those of background (Fig. 7) again shows a very marked a.c. base current depression before the first d.c. oxidation peak and a much less pronounced depression at potentials positive of the first d.c. peak. The presence of the large d.c. post-peaks coupled with the effects of guanine on the alternating base current very clearly confirms the view that guanine is strongly adsorbed at the graphite electrode and that the product(s) of guanine oxidation[1] are either not adsorbed or are adsorbed much less strongly than guanine itself.

Development of analytical methods

The concentration studies, scan rate studies and alternating current voltamme-

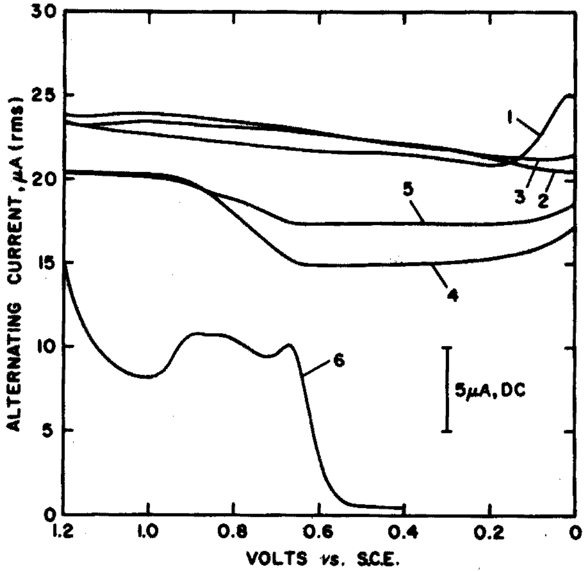


Fig. 7. A.c. and d.c. voltammograms of 0.40 m*M* guanine in McIlvaine buffer pH 7. Scans 1, 2, 3 are a.c. background traces, scans 4 and 5 are a.c. traces in the presence of guanine and scan 6 is a d.c. voltammogram. Scan rate, 5 mV sec^{-1}; alternating voltage, 10 mV peak-to-peak; 100 Hz; pyrolytic graphite electrode geometric area, 12.5 mm^2.

TABLE I

D.C. VOLTAMMETRIC DETERMINATION OF GUANINE IN THE PRESENCE OF 2.5 m*M* GUANOSINE[a]

Guanine concn. (*mM*)	*Peak current for guanine*		i_p/C ($\mu A\,mM^{-1}$)
	Range[b] (μA)	*Average* (μA)	
1 *M Acetic acid pH* 2.3			
0.0506	1.09–1.37	1.29	25.56
0.1012	2.32–2.42	2.35	23.26
0.2024	4.07–4.44	4.22	20.83
0.3036	5.99–6.24	6.11	20.11
0.4048	7.84–7.99	7.89	19.49
0.5060	9.64–9.84	9.71	19.18
McIlvaine pH 4			
0.0487	1.24–1.52	1.32	27.01
0.0975	2.34–2.37	2.36	24.21
0.1950	4.46–4.79	4.67	23.95
0.2924	6.65–7.15	6.87	23.48
0.3899	9.14–9.49	9.27	23.78
0.4874	11.52–11.97	11.70	24.00
McIlvaine pH 7			
0.0405	0.73–0.80	0.76	18.75
0.0811	1.56–1.66	1.59	19.66
0.1621	2.86–3.04	2.97	18.32
0.2432	4.36–4.54	4.45	18.31
0:3242	5.26–5.49	5.35	16.50
0.4053	6.31–6.81	6.59	16.25

[a] Geometric area of pyrolytic graphite electrode: 12.5 mm². [b] A minimum of three determinations at each concentration was run.

try discussed above, show that guanine is strongly adsorbed at the pyrolytic graphite electrode, but that in the presence of 5–15-fold amounts of guanosine the adsorbed guanine is virtually completely displaced from the electrode surface and that the electrooxidation of guanine becomes effectively diffusion-controlled. In a real analysis for guanine in the presence of guanosine, it would not be possible by spectral studies to decide the relative concentrations of guanine and guanosine. Thus it was decided to prepare i_p *vs.* C curves for guanine with sufficient guanosine present to ensure a 5-fold amount of guanosine, even at the highest possible concentration of guanine. At most pH values between pH 2 and 7 the maximum solubility of guanine is *ca.* 0.5 m*M* (super-saturated solutions slightly higher can be prepared, *e.g.*, in 1 *M* acetic acid, but such solutions would not normally be encountered in practice), and accordingly, all guanine solutions had sufficient guanosine added to make them 2.5 m*M* in guanosine. Actually, in McIlvaine buffer pH 4 and 7, guanosine is not soluble to this extent and the test solutions accordingly were run in the presence of undissolved suspended guanosine, *i.e.*, a saturated solution of guanosine. Under these conditions the voltammetric peaks of guanine were still very well defined and reproducible. Typical analytical data are presented in Table I and Fig. 8. In all three background

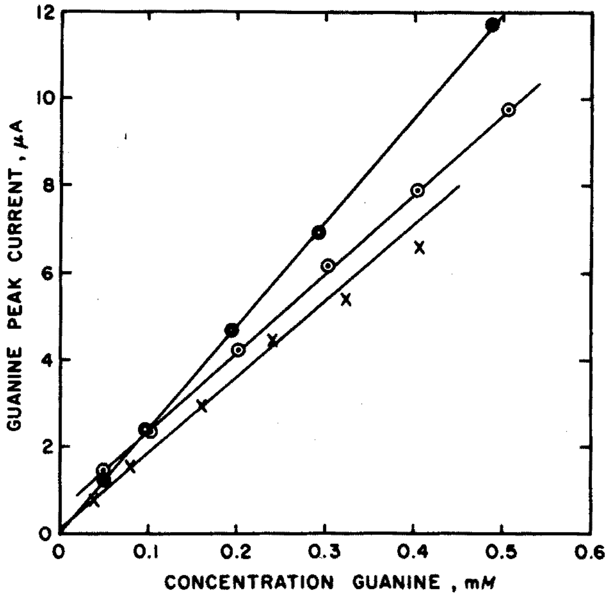


Fig. 8. Linear current *vs.* concentration curves for the voltammetric oxidation of guanine at the pyrolytic graphite electrode in the presence of 2.5 m*M* guanosine. (–○–) 1 *M* acetic acid pH 2.3 background; (–●–) McIlvaine buffer pH 4; (– × –) McIlvaine buffer pH 7.

electrolyte systems examined, linear i_p *vs.* C plots were obtained. The data obtained in both McIlvaine buffers pH 4 and 7 show curves that pass through the origin. This suggests that, under the conditions employed for this determination, the electrooxidation of guanine is diffusion-controlled. However, at guanine concentrations above *ca.* 0.3 m*M* in McIlvaine buffer pH 7, the guanine oxidation peak shifts very close to the rising portion of the guanosine oxidation peak and actually occurs as an inflection rather than a true peak. This results in a lack of precision in measuring the guanine current which is reflected in the data presented for such concentration levels.

In 1 *M* acetic acid a good linear i_p *vs.* C curve is obtained which does not pass through the origin. This implies that a small amount of guanine might still be adsorbed. The slight differences in the slope and current values for i_p *vs.* C curves in the three background electrolytes are no doubt due to minor adsorption phenomena and small changes in the diffusion coefficient for guanine. Nevertheless, all three systems examined are perfectly useful for analytical purposes. Clearly this method is readily capable of determining guanine in the presence of greater than 50-fold amounts of guanosine. In fact, it was noted in this study that many commercial samples of guanosine contained 0.5–1% of guanine.

Although no attempt was made to determine both guanine and guanosine in mixtures, this could readily be accomplished by determining the total guanine plus guanosine concentration spectrophotometrically in any of the three background systems employed. Then, the guanine concentration could be determined voltammetrically. Simple calculations would allow the individual concentrations of guanine and guanosine to be determined.

The author would like to express his thanks to the National Science Foundation and Research Corporation for supporting the work described.

SUMMARY

Guanine and guanosine are both electrochemically oxidized at the pyrolytic graphite electrode in aqueous solution. D.c. voltammetric concentration and scan rate studies and alternating current voltammetry have shown that both guanine and guanosine are adsorbed at this electrode. Adsorption of the compounds causes non-linear concentration *vs.* peak current curves, an increase in the voltammetric peak current function with scan rate and pronounced depressions of the alternating base current for pure solutions of both compounds. In the presence of guanosine, adsorbed guanine is displaced from the electrode surface, resulting in a decrease in the guanine d.c. voltammetric peak current. The extent of this decrease depends upon the relative concentrations of guanine and guanosine. Complete replacement of adsorbed guanine by guanosine appears to occur when greater than a 5-fold amount of guanosine is present. The electrooxidation of guanine then becomes diffusion-controlled. A simple and rapid determination of guanine in the presence of guanosine has been developed; a large amount of guanosine is added to the mixture, and the current for the guanine voltammetric oxidation peak is measured.

RÉSUMÉ

Guanine et guanosine sont toutes deux oxydées électrochimiquement à l'électrode de graphite pyrolytique, en solution aqueuse. On constate qu'il y a adsorption de ces deux substances sur l'électrode. En présence de guanosine, il y a déplacement de la guanine adsorbée; ce qui produit une variation de courant voltammétrique, fonction des concentrations relatives de guanine et guanosine. On propose une méthode de dosage simple et rapide de la guanine en ajoutant un excès de guanosine.

ZUSAMMENFASSUNG

Guanin und Guanosin werden beide in wässriger Lösung an der pyrolytischen Graphitelektrode elektrochemisch oxidiert. Gleichstromvoltammetrische Anreicherung, Untersuchungen zur Spannungsänderungsgeschwindigkeit und Wechselstromvoltammetrie ergaben, dass sowohl Guanin als auch Guanosin an dieser Elektrode adsorbiert werden. Die Adsorption der Verbindungen verursacht nichtlineare Konzentration–Strom-Kurven, eine grössere Abhängigkeit des voltammetrischen Spitzenstroms von der Spannungsänderungsgeschwindigkeit und eine deutliche Herabsetzung des Wechselgrundstroms bei reinen Lösungen beider Verbindungen. In Gegenwart von Guanosin wird das adsorbierte Guanin von der Elektrodenoberfläche verdrängt, was zu einer Verringerung des gleichstromvoltammetrischen Spitzenstroms des Guanins führt. Das Ausmass dieser Verringerung hängt von den relativen Konzentrationen von Guanin und Guanosin ab. Das adsorbierte Guanin scheint vollständig durch Guanosin ersetzt zu werden, wenn mehr als die 5-fache Menge Guanosin vorhanden ist. Die Elektrooxidation des Guanins wird dann diffusionsbestimmt. Es wurde eine einfache und schnelle Methode zur Bestimmung von Guanin in Gegenwart von Guanosin entwickelt; es wird eine grosse Menge Guanosin zum Gemisch gegeben und der Strom für die voltammetrische Oxidation des Guanins gemessen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COULOMETRIC DETERMINATION OF URANIUM AND IRON–URANIUM MIXTURES WITH FEEDBACK-CONTROLLED ELECTROLYSIS CURRENT

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(Received 21st June 1971)

The constant-current coulometric determination of uranium has been described by both reduction and oxidation methods. In an early paper[1], samples of uranium were reduced by passage through a cadmium reductor and collected in a known excess of iron(III) ammonium sulfate, and the resulting iron(II) was coulometrically oxidized in the presence of a cerium(III) sulfate intermediate. By this method, an accuracy and precision of ±0.6% was obtained with 2.5-mg samples of uranium. Another oxidimetric method has been described[2] in which 40-mg quantities of uranium are determined with high precision by first reducing the U(VI) to U(IV) with titanium(III) solution, destroying the excess of titanium(III), adding a solution which contains iron(III) sulfate and cerium(III) sulfate, and coulometrically oxidizing the iron(II) which is formed. The coulometric reduction of uranium(VI) in the presence of a titanium(III) intermediate has also been described[3]. Uranium was titrated successfully by this method in the presence of vanadium[4], but in the presence of both iron and vanadium the method was unsuccessful. Lingane[5] devised a novel method for the reductimetric determination of uranium in which the potential of the generating electrode is maintained at a constant value negative enough to reduce the U(VI) to a mixture of U(III) and U(IV). The U(III) thus functioned as a quasi-intermediate and aided in the reduction of U(VI) to U(IV).

These methods have not been widely adopted, partly because they are subject to interference from iron (and hence plutonium) and partly because very good controlled-potential coulometric methods exist for determining uranium[6-8]. The problem of determining uranium in the presence of iron (or plutonium) and uranium and iron together in the same matrix persists, however, and so it seemed appropriate to investigate the use of feedback-controlled coulometric titrimetry for these determinations. A method for the sequential oxidimetric titration of both uranium and iron in mixtures of the two metals has been developed. Determinations have been made on microgram and milligram amounts of uranium and iron with a recently developed coulometric titrator[9].

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* Oak Ridge National Laboratory is operated for the U.S. Atomic Energy Commission by the Union Carbide Corporation.

EXPERIMENTAL

Apparatus

The titrator which was used in these determinations has been described earlier[9,10]. The calibration of the electronic integrator was accomplished with the use of a Darcy Digital Multimeter Model 440 and a Standard Electric Time Co. (capacity 1000 sec with 0.1 sec divisions, Model S10) electric stopclock. The x-y recorders used were a Varian Model F-100 with a 7 × 10-in. chart and a Moseley Autograf 2D-2A with a 10 × 14-in. chart. The first recorder was used to record log cell current *vs.* indicator electrode potential and the second recorder plotted the indicator electrode potential *vs.* integrator readout potential. The electrolysis cell that was used was identical to the one described previously[9,10] with platinum generating, auxiliary, and indicator electrodes and a saturated calomel reference electrode (S.C.E.). The cell solution was stirred with a magnetic stirring bar encapsulated in heat-shrinkable Teflon tubing. All titrations were done under scrubbed and humidified nitrogen purge-gas. Solutions were added to the cell with calibrated micropipets.

Reagents

The cerium(III) sulfate–sulfuric acid solution was prepared from $(NH_4)_4$-$Ce(SO_4)_4 \cdot 2H_2O$ (Baker and Adamson). The cerium(IV) sulfate was reduced by an excess of hydrogen peroxide. Mallinckrodt $CrK(SO_4)_2 \cdot 12H_2O$ was used to prepare the stock chromium(III) sulfate solution. This solution was reduced to chromium(II) sulfate by passage through a Jones reductor column of 20 mesh amalgamated zinc (Mallinckrodt). Uranium standards were prepared from N.B.S.-certified U_3O_8 of 99.94% purity. The oxide was dissolved in nitric acid and the solution was evaporated to fumes twice with sulfuric acid.

Procedure

The use of the coulometric titrator with feedback-controlled electrolysis current has been previously described[9,10]. The integrator was carefully adjusted for zero drift in the output potential before a series of titrations. The integrator was electronically calibrated to ±0.02% with a 10–20 ohm resistor between the generating and auxiliary cell leads. The intermediate electrolyte was added to the cell and was preoxidized to a small excess of cerium(IV) to destroy traces of hydrogen peroxide. The iron and uranium were then pipeted into the cell and a quantity of chromium(II) sulfate prereductant was transferred to the cell from the Jones reductor. The micropipet that was used to add the prereductant was not allowed to touch the cell contents and it was not rinsed. The exit port tube was fitted into the hole in the cell top and the exiting nitrogen was bubbled through water to maintain a pressure of 3–4 cm water in the cell. The integrator was set to "Record-Operate", the "Stand-by—Titrate" switch was set to "Titrate" and the "Initial Current" was manually increased. The values of the "Set Potentials" were selected to correspond to current minima. As the titration proceeded the digital voltmeter stopped sampling the integrator readout potential automatically when the various "Set Potentials" were reached. The integrator readout was recorded at each of the three inflection-points and the amounts of uranium and iron found were calculated from the potential differences in the integrator readout. The iron present in both the intermediate and the prereductant was determined by the least-squares analysis described previously[9,10]. No corrections were made for a uranium blank or possible current inefficiencies. In most cases, the first titration of a series was considerably different from the remaining ones in the series and was discarded at the 99.9% confidence level. The most probable reason for this statistically erroneous titration is a trace of oxygen in the cell. It was assumed that the true equivalence-points in the titrations corresponded to the potential inflection-points, *i.e.*, corresponded to current minima in the titrating current.

RESULTS AND DISCUSSION

In the development of the recommended procedure the concentrations of both sulfuric acid and cerium(III) sulfate were varied. It was found that at sulfuric acid concentrations above 0.2 *M*, the breaks in the titration curve did not correspond to stoichiometric end-points at room temperature. When the solution acidity was reduced to *ca.* 0.08 *M* sulfuric acid the shape of the replicate titration curves between additions of prereductant changed very little. A solution containing nominally 2.4 mg of uranium and 1.5 mg of iron was prepared and was titrated repeatedly to obtain a measure of the replicate titration precision which was possible in 0.08 *M* sulfuric acid–0.03 *M* cerium(III) sulfate without involving the preparation of accurate standards. A series of 11 titrations was run, each titration yielding a determination for uranium and a determination for iron. The standard deviation for the uranium determination was found to be less than 4.0 μg. The standard deviation for the iron determination was found to be less than 1.5 μg. This precision was encouraging, hence an accurate uranium standard was obtained and determined in 0.08 *M* sulfuric acid–0.03 *M* cerium(III) sulfate. The results of that series of determinations are shown in Table I. Also shown in Table I are the results of a series of determinations of a 5-μg sample of uranium. The blank was quite large in this determination; uranium was intentionally added to make the determination of the blank repeducible. With this particular chemical system it was found to be advantageous to have 15 μg of uranium present in order to have a reproducible blank. The standard deviation(s) in the determination of the microsample of uranium is indicative of the reproducibility of

TABLE I

DETERMINATION OF URANIUM IN 0.08 *M* H_2SO_4–0.03 *M* $Ce_2(SO_4)_3$

Determination number	*Uranium found (mg)*	*Determination number*	*Uranium found (μg)*
1	2.041	1	4.76
2	2.043	2	5.12
3	2.043	3	5.36
4	2.044	4	4.52
5	2.042	–	—
6	2.042	–	—
Mean	2.043	Mean	4.94
s	0.001	*s*	0.38
s_r	0.05%	s_r	7.7%
Amount added	2.044	Amount added	5.10

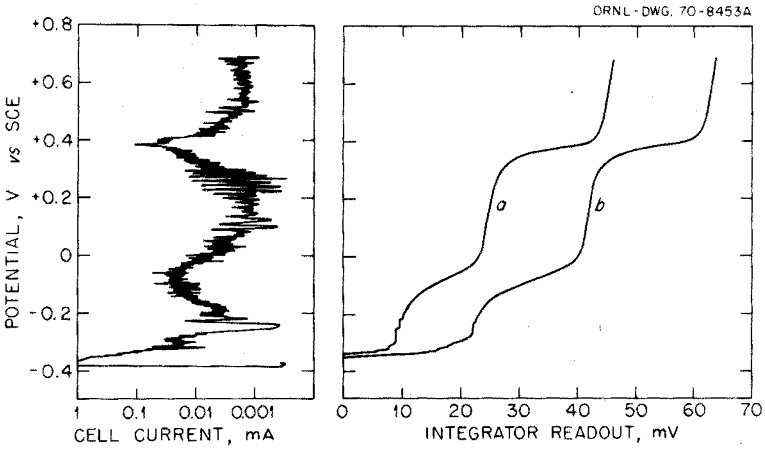


Fig. 1. Microdetermination of uranium. Oxidation of U(IV) to U(VI). Medium: 0.023 M $Ce_2(SO_4)_3$–0.08 M H_2SO_4. Solution volume: 6.5 ml. Integrator calibration: 9.742 μeq V^{-1}. (a) Uranium blank (154 neq); (b) uranium sample and blank (197 neq). Log cell current profile refers to curve b. $T = 28°$.

the blank, *i.e.*, 400 ng of uranium. Figure 1 shows typical titration curves that were obtained in the determination of 5 μg of uranium.

The precision and accuracy of the titration procedure were improved by further decreasing the concentration of sulfuric acid. Standards of iron and uranium were prepared and titrated in 0.01 M sulfuric acid–0.03 M cerium(III) sulfate. The slope of the titration curve in the region of the uranium end-point was increased from 2.1 mV μeq^{-1} in 0.08 M sulfuric acid to 28 mV μeq^{-1} in 0.01 M sulfuric acid. This increased slope produced greater reproducibility and accuracy in both the uranium and iron determinations (Table II).

TABLE II

DETERMINATION OF IRON–URANIUM MIXTURES IN 0.01 M H_2SO_4–0.03 M $Ce_2(SO_4)_3$

Determination number	*Uranium found (mg)*	*Iron found (mg)*
1	4.6938	1.0579
2	—	1.0579
3	4.6953	1.0578
4	4.6972	1.0576
5	4.6925	1.0582
Mean	4.6947	1.0579
s	0.0019	0.0002
s_r	0.04%	0.02%
Amount added	4.6935	1.0576

A series of titrations was then run of a mixture containing 4.7 mg of uranium and 1 mg of iron. The titration curves in Fig. 2 illustrate the various shapes of titration curves which were produced at various settings of the "Feedback Gain Function",

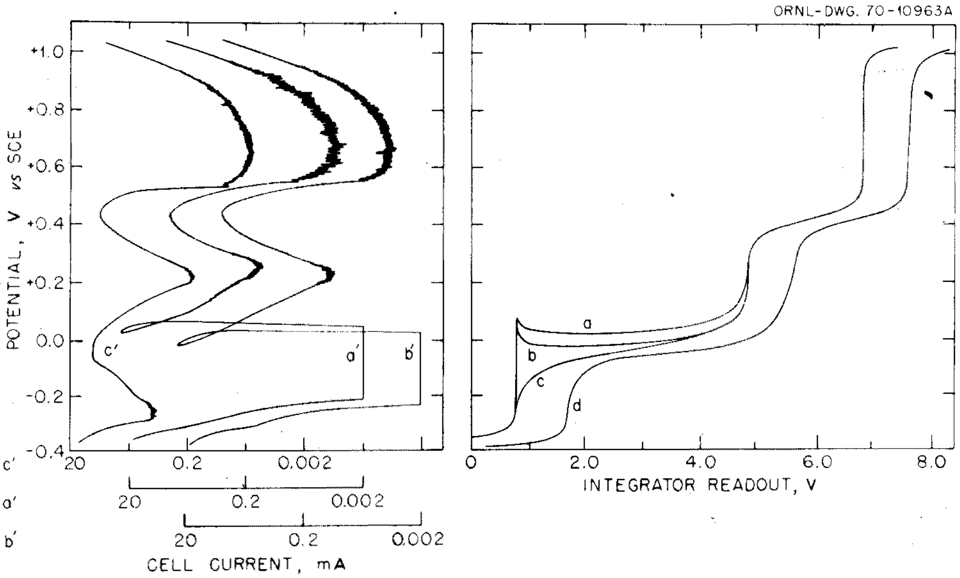


Fig. 2. Titration of iron–uranium mixtures at various "R_f" values. Medium: 0.01 M H_2SO_4–0.03 M $Ce_2(SO_4)_3$. Solution volume: 7 ml. Integrator calibration: 9.742 μeq V^{-1}. "R_f" values: (a) 40 ohms; (b) 50 ohms, (c) 90 ohms. Curve d was made using a constant 3.5 mA cell current. $T = 28°$.

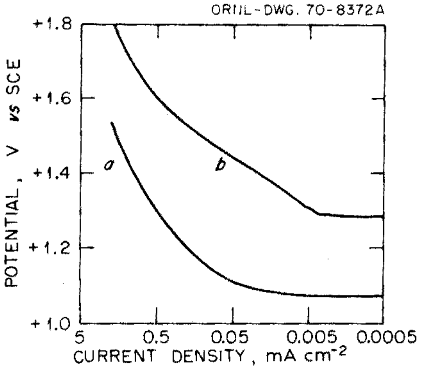
"R_f". The most obvious difference among the titration curves is the behavior of the indicator electrode potential after the chromium(II) end-point. This behavior was observed only when uranium was present and can be attributed to the lack of sufficient U(V) and U(VI) to poise the indicator electrode. The indicator electrode responded instead to the more reversible couples: Cr(II)–Cr(III), Fe(II)–Fe(III), and Ce(III)–Ce(IV). This behavior allowed the indicated potential to drift upwards until the potential buffer effect from the substantial quantity of iron(II) decreased the rate of potential change. At this point the titrating current began to increase. Shortly, there were sufficient quantities of U(V) and U(VI) present to poise the indicator electrode at a lower potential than that indicated. The potential decreased and the titrating current increased to a value greater than that set by the "Initial Current" control because of the positive feedback nature of the situation.

When the value of "R_f" was low, the potential drifted to a more positive value than when "R_f" was high. An arbitrary "R_f" of 80 ohms was used in the iron–uranium mixture determinations listed in Table II. This value was used because over-production of cerium(IV) before the chromium(II) end-point was avoided. The use of this "R_f" value also prevented excessive titrating currents in the positive feedback region following the chromium(II) end-point.

The titration curve of the iron–uranium mixture for constant titrating current of 3.5 mA is also shown in Fig. 2. This magnitude of cell current was chosen because the time required for this titration was equal to the time required in the same titration with feedback-controlled current with an "R_f" value of 80 ohms and an "Initial Current" setting of 16 mA. The slope of the titration curve in the region of the end-points was much less for this constant-current method than when controlled current was used.

In order to diminish the blank in the titration of uranium and to render the blank determination more reproducible, two configurations of the auxiliary electrode assembly were examined. One configuration consisted of a platinum wire dipping into a solution of 20% sulfuric acid separated from the cell solution by a porous Vycor frit. Because of possible hydrogen diffusion through the frit into the bulk solution, a two-stage auxiliary electrode configuration was tested. The first stage—a silver wire dipping into a solution of 4 *M* silver perchlorate and 1:3 perchloric acid—was separated from a second stage by a porous Vycor plug. The second stage was separated from the bulk solution by a second porous Vycor plug. The blanks produced with both the above systems were of the same order of magnitude and the resistances of both cells were about the same. According to Goode *et al.*[2], the blank could be reduced by replacing the platinum generating electrode with a gold-foil electrode. In the present work, titrations of uranium with a gold anode resulted in brown deposits in the cell and erratic titration behavior. The use of a gold anode appeared to have no advantage and its use was soon abandoned.

It has been mentioned previously that the current efficiency for the generation of cerium(IV) from cerium(III) sulfate was dependent on the concentration of sulfuric acid and generally decreased at both low and high current densities[11]. The generation efficiency for cerium(IV) in 0.03 *M* cerium(III) sulfate was evaluated in both 0.01 and 0.08 *M* sulfuric acid. A plot of generating electrode potential *vs.* current density in 0.01 *M* sulfuric acid is shown in Fig. 3. A similar plot for a solution that was 0.08 *M* in sulfuric acid is shown in Fig. 4. The current efficiency was clearly less in 0.01 *M* sulfuric acid, but the increased sharpness of the end-point made the 0.01 *M* sulfuric acid–0.03 *M* cerium(III) sulfate medium an advantageous choice. The overall titration efficiency that was observed was higher than that expected from the curves of Figs. 3 and 4. This efficiency was probably due to the dual intermediate condition, cerium(III) and iron(II), when uranium(IV) was being oxidized, and to some direct oxidation of uranium(IV) at the platinum electrode. According to Figs. 3 and 4, there should be no decrease in current efficiency at low current densities.



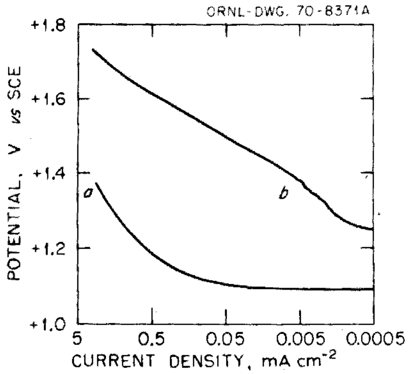


Fig. 3. Electrode potential–current density profile. (a) 0.01 *M* H_2SO_4–0.03 *M* $Ce_2(SO_4)_3$; (b) 0.01 *M* H_2SO_4. Electrode material: platinum. $T = 28°$.

Fig. 4. Electrode potential–current density profile. (a) 0.08 *M* H_2SO_4–0.03 *M* $Ce_2(SO_4)_3$; (b) 0.08 *M* H_2SO_4. Electrode material: platinum. $T = 28°$.

CONCLUSIONS

A method has been developed for the determination of uranium and iron by the electrolytic oxidation of uranium(IV) and iron(II) in the presence of a cerium(III) sulfate intermediate at room temperature with the feedback-controlled coulometric titrator. The effect of changes of feedback gain ("R_f" setting) on the shape of the titration curves has been illustrated. Generation efficiency for cerium(IV) in the media studied does not appear to decrease at very low current densities. This method of determination was shown to be extremely accurate as long as the concentration of sulfuric acid was less than 0.1 *M*.

One of the authors (J.E.M.) wishes to acknowledge financial support in the form of a predoctoral fellowship from Oak Ridge Associated Universities.

SUMMARY

The determination of uranium and iron mixtures has been accomplished by feedback-controlled electrolytic oxidation in the presence of a cerium(III) sulfate–sulfuric acid intermediate electrolyte. Samples were prereduced with an excess of chromium(II) to a mixture of U(III), U(IV) and Fe(II). The uranium was then determined by conversion of U(IV) to U(VI), and the Fe(II) was determined by oxidation to Fe(III). The progress of these titrations was followed by zero-current potentiometry with a platinum indicator electrode. Determinations of 5-mg quantities of uranium can be made with a precision of 0.04%; at the 5-μg level the precision is 4.5%. In the presence of 5 mg of uranium, determinations of 1-mg amounts of iron were made with an accuracy and precision of ±0.02%.

RÉSUMÉ

On propose un dosage coulométrique de mélanges uranium–fer, par oxydation électrolytique contrôlée, en retour, en présence d'un électrolyte intermédiaire sulfate de cérium(III)–acide sulfurique. On procède à une réduction préalable de l'uranium et du fer par le chrome(II) en excès. L'uranium et le fer sont ensuite dosés par oxydation de l'uranium(IV) en uranium(VI), et du fer(II) en fer(III). Le titrage s'effectue par potentiométrie à courant nul, en utilisant une électrode indicatrice de platine. On peut ainsi doser 5 mg d'uranium avec une précision de 0.04%; avec des quantités de 5 μg, la précision est de 4.5%. Il est possible de doser 1 mg de fer, en présence de 5 mg d'uranium, avec une exactitude et une précision de ±0.02%.

ZUSAMMENFASSUNG

Uran- und Eisengemische wurden durch rückkopplungsgeregelte elektrolytische Oxidation in Gegenwart von Cer(III)-sulfat–Schwefelsäure als Zwischenelektrolyt bestimmt. Die Proben wurden mit überschüssigem Chrom(II) zu einem Gemisch von U(III), U(IV) und Fe(II) vorreduziert. Das Uran wurde dann durch Oxidation von U(IV) zu U(VI) und das Fe(II) durch Oxidation zu Fe(III) bestimmt. Der Ablauf dieser Titrationen wurde durch Nullstrompotentiometrie unter Verwendung einer

Platin-Indikatorelektrode überwacht. 5 mg Uran können mit einer Reproduzierbarkeit von 0.04% bestimmt werden; im 5 μg-Bereich ist die Reproduzierbarkeit 4.5%. In Gegenwart von 5 mg Uran wurde 1 mg Eisen mit einer Genauigkeit und Reproduzierbarkeit von ±0.02% bestimmt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

TITRIMETRIC DETERMINATION OF URANIUM WITH FLUORIMETRIC END-POINT DETECTION

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(Received 16th May 1971)

Various procedures based on fluorescence have been used in analyses for uranium(VI), but fluorescence does not seem to have been utilized in titrations of uranium. It was considered that titration of uranium with fluorimetric end-point detection would lead to a selective and sensitive determination of this element.

Many titrimetric procedures have been proposed for the determination of uranium. Most of them are based on the reduction of uranium(VI) to uranium(IV) by means of a metallic reductor with subsequent oxidimetric titration. Nearly all methods are restricted to concentrations larger than 10^{-3} *M*. Only one paper[1] describes the determination of 10^{-5} *M* uranium by coulometry at constant potential. Various reagents can be applied for the reduction of uranium to the tetravalent state and for the subsequent oxidimetric titration. In this investigation, the only procedures examined were the Jones-reductor followed by a titration with cerium(IV), and reduction with iron(II) in phosphoric acid medium followed by oxidation with potassium dichromate.

Two possibilities for fluorimetric indication were tried, based on the fluorescence of uranium(VI) and cerium(III), respectively. The former has the advantage of a better selectivity, whereas the latter is much more sensitive.

EXPERIMENTAL

The experiments were carried out on a Jobin et Yvon spectrofluorimeter (type Bearn, Xenon lamp type XBO 150 W/1) with two monochromators. A quartz cell of 2 × 2 × 4 cm was used with the fluorimeter. The addition of titrant was effected with a piston-type 0.5-ml microburet. The contents of the cell were stirred magnetically.

Wavelength settings

In sulphuric acid solution, the wavelengths for the excitation and fluorescence radiation resulting in the largest sensitivity were 285 nm and 515 nm, respectively, for uranium(VI), and 259 nm and 362 nm for cerium(III).

In 10.5 *M* phosphoric acid solutions, the wavelengths for excitation and fluorescence were 322 nm and 508 nm, respectively.

Titrations in sulphuric acid solution

Procedure based on fluorescence of cerium(III). Reduce 10 ml of a solution containing 20 μg–1 mg of uranium(VI) in a Jones-reductor (amalgamated zinc with

2.5–3% mercury; column diameter 1 cm, length 10 cm). Adjust the flow to 3 ml min^{-1}. Wash the column 5 times with 15-ml portions of 1 *M* sulphuric acid. Collect the effluent in a 100-ml measuring flask and dilute to the mark with 1 *M* sulphuric acid.

Transfer 10 ml of the resulting solution to the titration cell and titrate with the appropriate (10^{-3} or 10^{-2} *M*) solution of cerium(IV) in 0.2 *M* sulphuric acid. Use suitable amounts of titrant so that 5–6 measurements of the fluorescence can be done before and after the equivalence point. Determine the equivalence point by the intersection of the two straight parts of the titration curve.

Procedure based on fluorescence of uranium(VI). The same procedure can be applied as in the previous case except that the original solution should contain at least 200 μg of uranium. This is because the fluorescence of uranium(VI) is less intense than that of cerium(III).

RESULTS AND DISCUSSION

Titration in sulphuric acid solution

The results of the titrations based on cerium(III) fluorescence appeared to be accurate. The precision depended on the concentration. The standard deviation for 200 μg of uranium in the original solution, corresponding to 20 μg in the titration solution, which was 10^{-5} *M*, was 1.8% (from 12 determinations). For 100 μg the standard deviation was 3% ($n=5$) and for 20 μg (10^{-6} *M* in the titration solution) 15% ($n=12$). When uranium(VI) fluorescence was utilized, the determination of 200 μg of uranium was possible with good accuracy, the standard deviation being 3.6% ($n=10$).

In both procedures no uranium(III) was observed in the effluent; obviously, any trivalent uranium leaving the column is immediately oxidized by air at the concentration levels used under these conditions. The sulphuric acid concentration in the titration solution should be in the range 0.2–1 *M*. However, when the fluorescence of uranium(VI) is utilized, a sulphuric acid concentration of 1 *M* sulphuric acid has to be preferred, as is clear from Fig. 1.

Interferences

Few ions interfere with the determination of uranium in sulphuric acid solution. In both procedures 100-fold amounts of zinc, cadmium, aluminium, nickel, manganese, cobalt, carbonate and acetate and 10-fold amounts of lead and magnesium did not interfere. Interference by other ions or larger amounts of these ions may be caused in different ways. Larger amounts of lead cause coprecipitation of uranium with lead sulphate. Chloride, iodide and bromide interfere when present in equal amounts with uranium, because these ions strongly decrease the fluorescence.

Ions which are reduced in the reductor to compounds which can be oxidized by cerium(IV) may of course interfere, especially when end-point indication by cerium(III) fluorescence is applied. However, when compounds are formed which can easily be oxidized by air to compounds which do not react with cerium(IV), determinations are still possible with both indication methods. On the other hand, some ions may induce the oxidation of uranium(IV) by air. It has been shown recently[2] that there is no induction at about 10^{-3} *M* concentrations of uranium(IV). However, in 10^{-5} or 10^{-6} *M* solutions of uranium(IV) induced oxidation of uranium(IV) can take place.

Quite often, both effects may occur simultaneously, depending on the concentration of both uranium and the interfering ions. In general, the following can be stated with respect to interferences with the determination at the concentration level of uranium of 10^{-5}–10^{-6} M in the titration solution. Molybdenum, tungsten, tin and vanadium interfere. Equal amounts of titanium, chromium and copper can be tolerated. With titanium, end-point indication based on uranium(VI) is necessary as the oxidation of some titanium(III) precedes the oxidation of uranium(IV). This is not necessary in the case of chromium as all chromium(II) is oxidized to chromium(III) by air before the titration.

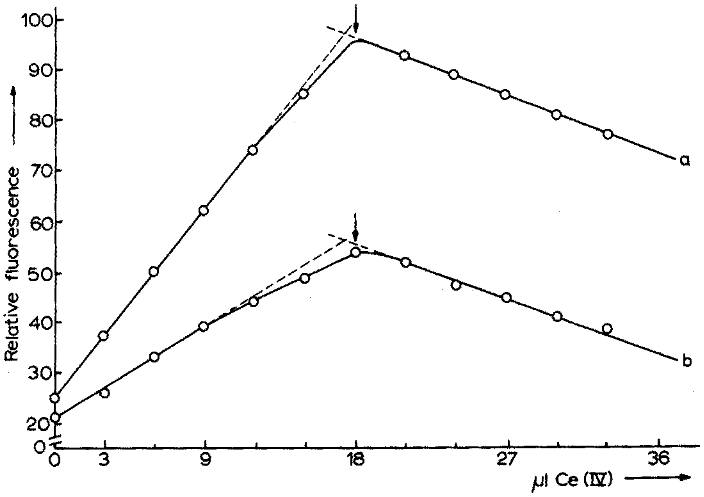

Fig. 1. Titration curve of 10 ml of 10^{-5} M uranium(IV) with 10^{-2} M cerium(IV) in (a) 1 M H_2SO_4; (b) 0.2 M H_2SO_4. Excitation wavelength 285 nm; fluorescence wavelength 515 nm; uranium(VI) fluorescence as indication.

Titration in the presence of iron causes difficulties. From the formal potentials it could be expected that the oxidation of uranium(IV) would precede the oxidation of iron(II). However, at the 10^{-5}–10^{-6} M level, this occurs only when the titration is carried out very slowly, so that the titration becomes impracticable. Therefore in the presence of iron the determinations were carried out in phosphoric acid medium (see below).

Titrations in phosphoric acid solution

It is well known that uranium(VI) can be reduced by iron(II) in phosphoric acid solution. A direct titration with iron(II) has been described, as well as a back-titration with potassium dichromate after addition of iron(II) in excess[3]. These titrations can also be carried out with fluorimetric end-point detection, although with rather poor precision.

The fluorescence of uranium(VI) in phosphoric acid solutions largely depends on the concentration of the acid. The best results were obtained in 10.5 M phosphoric acid. Direct titration of 200 μg of uranium(VI) in 10 ml of solution with iron(II) was possible with a standard deviation of 8%.

The main advantages of the procedure in phosphoric acid solution are that no column has to be used and that iron does not interfere. Titrations of uranium in the presence of iron(III) were carried out by the back-titration procedure and by direct titration with iron(II). Some results of direct titrations are given in Table I. In the case of the back-titration, the oxidation of the excess of iron(II) precedes the oxidation of uranium(IV) but the amount of uranium can easily be found from the titration curve, as is seen in Fig. 2.

TABLE I

DIRECT FLUORIMETRIC TITRATION OF 10^{-4} *M* URANIUM(VI)

(Reduction with iron(II) in 10.5 *M* phosphoric acid in the presence of iron(III). Excitation wavelength 322 nm, fluorescence wavelength 505 nm)

Fe(III) concn. (*M*)	*U(VI) (mg)*		*Standard deviation (%)* (*n* = 10)
	Present	*Found*	
10^{-4}	0.190	0.192	7
10^{-3}	0.190	0.192	7
10^{-2}	0.190	0.174	9

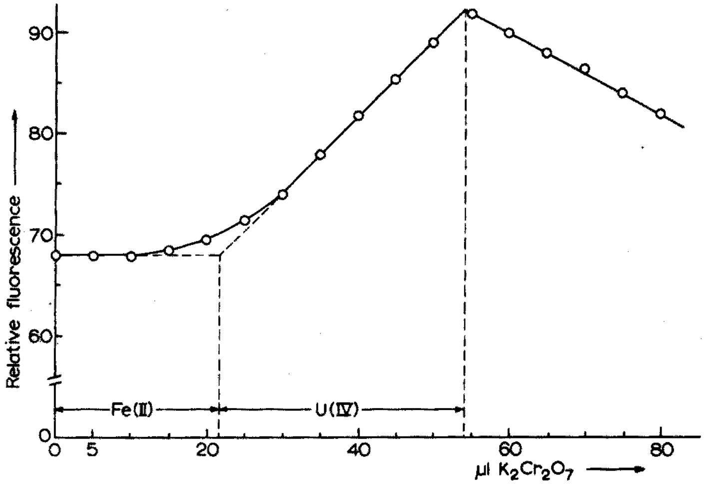

Fig. 2. Titration curve of 10 ml of 10^{-4} *M* uranium(VI) reduced with excess of iron(II) in 10.5 *M* H_3PO_4. Titrant 10^{-2} *M* dichromate. Excitation wavelength 322 nm; fluorescence wavelength 505 nm; uranium(VI) fluorescence as indication.

The advantage of fluorimetric indication over other methods of end-point indication in the titrimetric determination of uranium is that considerably lower limits of determinations can readily be achieved.

The authors wish to thank Mrs. Sheila Beijer for valuable experimental help.

SUMMARY

The determination of uranium based on reduction of uranium(VI) to uranium(IV) and subsequent oxidation titration can be done by fluorimetric end-point detection. In 0.2–1 *M* sulphuric acid solution, reduction by a Jones-reductor was followed by oxidation with cerium(IV). The fluorescence of either uranium(VI) or cerium(III) can be utilized, the fluorimetric titration of 10^{-5} *M* or 10^{-6} *M* solutions of uranium(IV), respectively, being possible. In 10.5 *M* phosphoric acid solution, uranium(VI) was reduced with iron(II), and uranium(IV) was titrated with dichromate. The limit of determination was 10^{-4} *M* in this case.

RÉSUMÉ

Le dosage de l'uranium, basé sur la réduction de l'uranium(VI) en uranium(IV) et titrage par réoxydation peut s'effectuer avec détection fluorimétrique du point final. La réduction s'effectue à l'aide d'un réducteur Jones, et le titrage au moyen de cérium(IV), en milieu acide sulfurique 0.2 à 1.0 *M*. On peut utiliser soit la fluorescence de l'uranium(VI), soit celle du cérium pour le titrage d'uranium(IV), respectivement 10^{-5} ou 10^{-6} *M*. En milieu phosphorique, l'uranium(VI) est réduit par le fer(II); l'uranium(IV) est titré par le dichromate. La limite de dosage dans ce cas est 10^{-4} *M*.

ZUSAMMENFASSUNG

Die Bestimmung von Uran auf der Grundlage der Reduktion von Uran(VI) zu Uran(IV) und anschliessender Oxidationstitration kann mit fluorimetrischer Endpunktsindizierung ausgeführt werden. Auf die mit einem Jones-Reduktor bewirkte Reduktion in 0.2–1 *M* schwefelsaurer Lösung folgte die Oxidation mit Cer(IV). Es kann die Fluoreszenz entweder von Uran(VI) oder von Cer(III) ausgenutzt werden, wobei 10^{-5} *M* bzw. 10^{-6} *M* Uran(IV)-Lösungen fluorimetrisch titriert werden können. In 10.5 *M* phosphorsaurer Lösung wurde Uran(VI) mit Eisen(II) reduziert und Uran(IV) mit Dichromat titriert. Die Bestimmungsgrenze in diesem Fall war 10^{-4} *M*.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE PRECISION AND ACCURACY OF SOME CURRENT METHODS FOR POTENTIOMETRIC END-POINT DETERMINATION WITH REFERENCE TO A COMPUTER-CALCULATED TITRATION CURVE

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(Received 27th May 1971)

In a recent article[1] the importance of computer calculation in the interpretation of the form of titration curves was demonstrated. It was shown how the main and side-reactions occurring in the different parts of a titration curve could be calculated and how the results could be used to determine the optimal titration conditions for a specific analytical problem. Once a suitable titration procedure has been selected, the analytical chemist is, however, faced with the problem of which method to use to evaluate the equivalence point. In the making of this choice the systematic error associated with each method is, of course, of prime importance, as is the estimated value of the precision of the method and the time required for a single determination of the equivalence point. It is our aim to illustrate the importance which computer calculation can play in the choice of the optimal method for the evaluation of the equivalence point from the titration curve. Since several different methods for evaluation are discussed, this article can also be regarded as providing a critical survey of the methods most frequently used to evaluate the equivalence point from potentiometric titration data.

The discussion is confined to a particular computer-calculated titration curve, namely that of fluoride with thorium nitrate. This titration provides a suitable example of an asymmetrical titration curve. Furthermore, the titration has been found, in practice, to yield reproducible titration data[2,3]. Similar discussions can, however, be applied to all titration curves for which the stability constants for the different species involved are fairly accurately known and in which the titration reactions are not slow.

SAMPLE TITRATION

Sodium fluoride (100 ml of 0.001 *M*) is titrated potentiometrically with v ml of 0.001 *M* thorium nitrate. The ionic strength is kept approximately constant at 0.1 *M*. The titration curve is registered by means of an Orion fluoride-selective lanthanum trifluoride membrane electrode which is known to obey the Nernst equation throughout the relevant pF range. The precision in the e.m.f. is estimated to be ± 0.05 mV (corresponding to ± 0.0008 pF units) at each titration point[3], and errors in the total volume of titrant added are neglected.

The form of the titration curve was calculated by the HALTAFALL program[4] for $v = 0, 0.05, 0.1, 0.15, \ldots 35$ ml assuming equilibrium at each titration point and using the stability constants specified in Table I. The concentrations of the different species

TABLE I

STABILITY AND SOLUBILITY CONSTANTS FOR THE Th^{4+}–F^-–H^+ SYSTEM (*cf.* ref. 21)

Equilibria	*Log of stab. constants*
$2\,H_2O + Th^{4+} \rightleftharpoons Th(OH)_2^{2+} + 2H^+$	− 9.1
$H_2O + 2\,Th^{4+} \rightleftharpoons Th_2OH^{7+} + H^+$	− 2.65
$2\,H_2O + 2\,Th^{4+} \rightleftharpoons Th_2(OH)_2^{6+} + 2\,H^+$	− 4.70
$3\,H_2O + 2\,Th^{4+} \rightleftharpoons Th_2(OH)_3^{5+} + 3\,H^+$	− 8.83
$14\,H_2O + 6\,Th^{4+} \rightleftharpoons Th_6(OH)_{14}^{10+} + 14\,H^+$	−36.53
$15\,H_2O + 6\,Th^{4+} \rightleftharpoons Th_6(OH)_{15}^{9+} + 15\,H^+$	−40.37
$Th^{4+} + F^- \rightleftharpoons ThF^{3+}$	7.62
$Th^{4+} + 2\,F^- \rightleftharpoons ThF_2^{2+}$	14.02
$Th^{4+} + 3\,F^- \rightleftharpoons ThF_3^+$	18.81
$H^+ + F^- \rightleftharpoons HF$	3.28
$H^+ + 2\,F^- \rightleftharpoons HF_2^-$	4.26
$ThF_4(s) \rightleftharpoons Th^{4+} + 4\,F^-$	−27.81

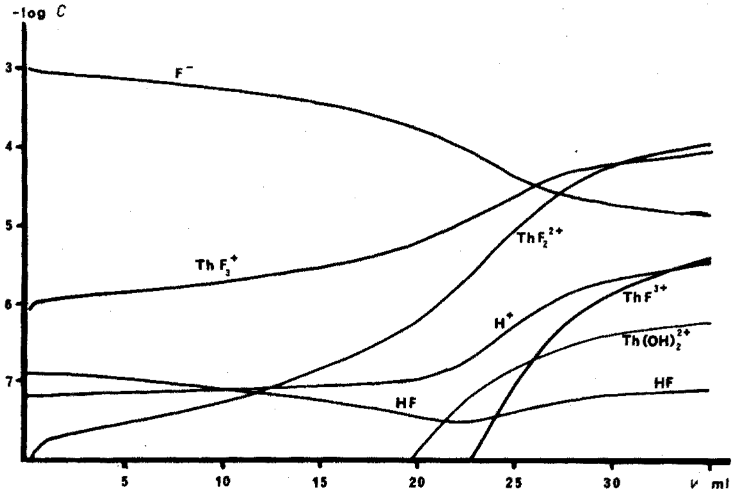

Fig. 1. The logarithmic concentrations of the different species formed in the titration of 100 ml of 0.001 *M* sodium fluoride with *v* ml of 0.001 *M* thorium nitrate.

involved in the titration are shown in Fig. 1. All calculations were performed with an accuracy[4] of 0.01 % in the total concentration of each component, *i.e.* Th^{4+}, F^-, and H^+. The calculated titration curve, *i.e.* pF_{calc} *versus* v ml of thorium nitrate added, is thus not in error by more than 0.03 %. This error has been neglected in the subsequent discussions. The form of the input data required by the computer program is in accordance with examples given by Dyrssen *et al.*[5,6].

Notation

v_0 = initial volume in titration vessel (= 100 ml).
v_{eq} = theoretical equivalence volume (= 25 ml).

v_{end} = end-point volume obtained by a specific evaluation method.
v_{infl} = inflection point volume.
% systematic error $= 100\,(v_{eq}-v_{end})/v_{eq}$.
% precision $= \pm\,100a/v_{eq}$, where a is the estimated precision in ml in the vicinity of the end-point.

Main types of evaluation methods

Many methods for the evaluation of potentiometric titration data have been suggested. Most of these are, however, either only applicable to specific problems or do not appear to have come into general use and are therefore not dealt with here. A large number of the most frequently used methods employ only the sigmoid form of a titration curve in the evaluation procedure, and thus disregard the fact that chemical equilibria and mass balance conditions are responsible for the form of a titration curve. Many evaluation methods are concerned with differences in potential between each new addition of titrant (differential methods) while others are based strictly on mass balance and equilibrium equations.

TABLE II

RESULTS FROM THE DIFFERENT METHODS DISCUSSED IN THIS ARTICLE

Method	*Systematic error (%)*	*Systematic error after correction for asymmetry (%)*	*Estimated precision (%)*	*Estimated time for one end-point evaluation (min)*	*Possible use of a computer*
Maximum slope	4.0	—	±0.7	3	Small
Tubbs[8]	3.0	—	±0.9	5	Small
Kohn–Zitko[9]	4.0	—	±0.3	3	Small
$\Delta E/\Delta v$	3.6	—	±0.6	7	Considerable
Cohen[10]	3.6	2.4	±0.3	9	Considerable
Kolthoff[11]–Hahn[12] –Fortuin[13]	5–10	—	—	5	Considerable
$\Delta^2E/\Delta v^2$	3.6	—	—	7	Considerable
$\Delta v/\Delta E$[14]	−0.8	—	±1.2	7	*cf.* Liteanu
Liteanu–Cörmös[15]		0–5	±0.9	20	Considerable
Cavanagh[16]–Herringshaw[17]	0.2	—	±4	7	Considerable
Pre-selected e.m.f.	Small	—	±0.5	5	Small
Gran[18]	Small	—	±0.2	7	Considerable
Multi-parameter	Small	—	±0.1	—	Must be used

The results obtained by the different methods discussed are summarised in Table II. Only a brief summary of each method is given in this article and for more detailed information the original papers should be consulted.

METHODS BASED ON THE SIGMOID FORM OF A TITRATION CURVE

When the primary titration data are exploited directly, errors in the e.m.f. reading are often of little importance for the total precision associated with the specific method. In order to obtain an approximate value for the precision of a given method, the evaluation was carried out by twelve different chemists in this laboratory using the primary titration curve shown in Fig. 2. The average deviation from the mean value (v_{end}) was then taken as a measure of the precision.

Maximum slope method

Probably the most frequently used method of evaluating the results from the titration curve is by visual estimation of the v value corresponding to the maximum slope of the titration curve. This procedure is illustrated by the vertical dotted line shown in Fig. 2. The computer calculations show that in this particular titration the difference between the inflexion and equivalence points[7] yields a systematic error of 4%. The precision of this method of evaluation was estimated as ±0.7%.

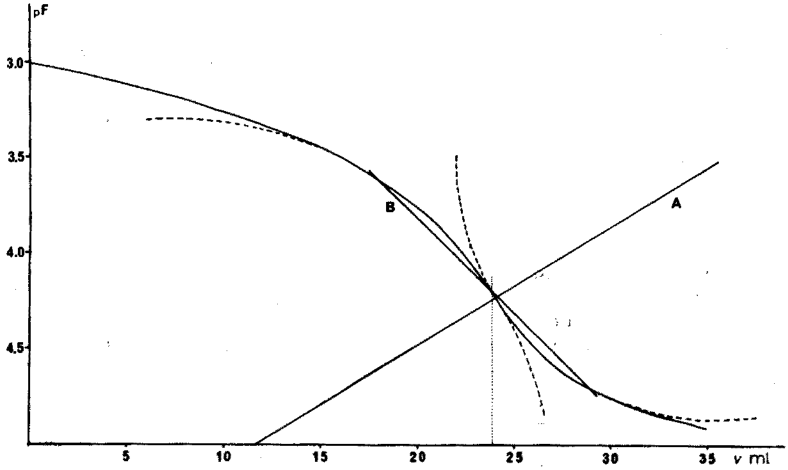

Fig. 2. Application of different end-point evaluation methods of the titration curve, pF *vs.* v ml of titrant, for the titration of 100 ml of 0.001 M sodium fluoride with v ml of 0.001 M thorium nitrate. The dotted line indicates the location of the point of maximum slope. Line A connects the centers of the two circles shown by dotted segments according to Tubbs' method. The two areas formed between line B and the pF *vs.* v ml curve are equal according to Kohn–Zitko's method.

Tubbs' method[8]

In this method the end-point is evaluated as the v value where the line connecting the centres of two circles intersects the titration curve. One of the circles is constructed to partly coincide with the sigmoid part of the titration curve for $v > v_{\mathrm{infl}}$ and the other circle is constructed in a similar way for $v < v_{\mathrm{infl}}$. The procedure is illustrated by the partly dashed circles and connecting line A shown in Fig. 2. The method yields, in this particular case, a systematic error of 3%, the precision being estimated as ±0.9%.

The Kohn–Zitko method[9]

In this method a straight line which intersects the primary titration curve at three points is constructed so that the two areas formed between the titration curve and the straight line are equal. The v value corresponding to the point where the two areas meet is then taken as the end-point. The procedure is illustrated by line B in Fig.

2. For this particular titration a systematic error of 4 % is obtained, while the precision was estimated as ±0.3 %.

DIFFERENTIAL METHODS

In differential methods the error in the e.m.f. reading is probably the most important precision-limiting factor. The estimated errors given below were therefore derived from this error only, *i.e.* ±0.05 mV.

Methods based on $\Delta E/\Delta v$ values

The $\Delta E/\Delta v$ method. In order to increase the precision in the evaluation of the inflexion point the ratios $\Delta E/\Delta v = (E_{n+1} - E_n)/(v_{n+1} - v_n)$ are plotted against $(v_{n+1} + v_n)/2$, where v_n and E_n denote the v and E values, respectively, in the nth titration point. The v value corresponding to the maximum on this curve is then taken as the end-point. This is illustrated by the solid curve in Fig. 3 where the maximum occurs for $v = 24.1$ ml.

An estimate of the precision can be made from the results of the computer calculations. Assuming the volume difference between two successive titration points to be 0.25 ml, the maximum deviation from the $\Delta E/\Delta v$ plot is given by the $\Delta E/\Delta v \pm 0.4$ curves in Fig. 3. From these two plots the precision was estimated to be ±0.15 ml, a value which is slightly better than the precision obtained by the maximum slope method.

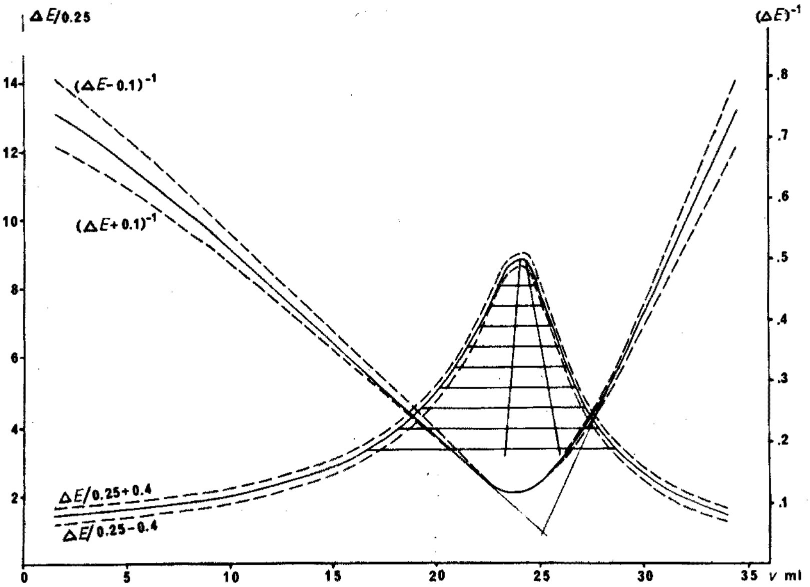

Fig. 3. The $\Delta E/0.25$, $\Delta E/0.25 \pm 0.4$, $1/\Delta E$ and $1/(\Delta E \pm 0.1)$ curves for the titration of 100 ml of 0.001 *M* sodium fluoride with v ml of 0.001 *M* thorium nitrate.

Cohen's method[10]. The aim of this method is to improve the precision in the location of the maximum on the $\Delta E/\Delta v$ plot. Several chords are drawn connecting points with the same $\Delta E/\Delta v$ values. The intersection of the best straight line through the mid-points of these chords with the $\Delta E/\Delta v$ plots is taken as the end-point. This is illustrated by the line through the mid-points of the chords in Fig. 3 which intersects the $\Delta E/\Delta v$ plot at 24.1 ml.

In order to correct for the difference between v_{eq} and v_{end}, Cohen suggests that, instead of dividing the chords into two equal parts they should be divided in the ratio 1:4 for a 1:4 reaction. The point of intersection of the best straight line through these points on the chords with the $\Delta E/\Delta v$ plot is equal to 24.4 ml, *i.e.* the systematic error decreases significantly (*cf.* Fig. 3).

The Kolthoff[11]*–Hahn*[12]*–Fortuin*[13] *methods.* This group of methods exploits titration data around the end-point. In the Fortuin method four titration points with the same Δv are selected. Ratios between the corresponding ΔE values are then calculated and the end-point is evaluated from the Fortuin nomograph.

It should be noted that Fortuin claims accurate values only for symmetrical titration curves. Even so, since the method is in frequent use, it was thought profitable to apply it to the example under study. Results based on different Δv values are:

v values used (ml)	*Δv(ml)*	*v_{end}(ml)*
15, 20, 25, 30	5	22.75
18, 22, 26, 30	4	23.40
20, 23, 26, 29	3	23.65
21, 23, 25, 27[a]	2	23.77
22, 23, 24, 25[a]	1	23.85

[a] Estimated values, Fortuin nomograph not applicable.

It is obvious that the estimated v_{end} value is strongly dependent on the Δv value chosen.

Second derivative. The intersection on the v axis of the plot $\Delta^2E/\Delta v^2$ locates the maximum on the $\Delta E/\Delta v$ plot, *i.e.* the inflexion point. In this example, a v value of 24.1 ml is obtained. Owing to the great error in the calculation of Δ^2E introduced by the e.m.f. error of ± 0.05 mV the precision will, however, be very poor. The method will thus not be further considered.

Methods based on $\Delta v/\Delta E$ values

The $\Delta v/\Delta E$ method. Gran[14] pointed out that when $\Delta E/\Delta v$ methods were applied in the evaluation of the end-point, one had to rely mainly on data close to the end-point. He thus suggested that the function $\Delta v/\Delta E = (v_{n+1} - v_n)/(E_{n+1} - E_n)$ be plotted against $(v_{n+1} + v_n)/2$. In this way two straight lines would be obtained, one before and one after the end-point. The v value corresponding to the point of intersection between these two lines ought then to correspond to the end-point. The $\Delta v/\Delta E$ plot ($\Delta v = 1$ ml) is illustrated by the solid curve in Fig. 3 which has a minimum value of 24 ml. If the linear parts of the two legs of the curve are extended, as is shown by the solid straight lines in Fig. 3, they intersect at a v value of 25.2 ml.

The $\Delta v/\Delta E$ plot is partly linear since,

$$(\mathrm{d}E)^{-1} \propto (\mathrm{d}\log[\mathrm{F}^-])^{-1} = [\mathrm{F}^-]$$

If the dilution effect is neglected the fluoride concentration decreases in proportion to the amount of thorium added for $v < v_{eq}$, *i.e.*

$$(\Delta E)^{-1} \propto v_{eq} - v$$

The $\Delta v/\Delta E$ methods are thus partly based on mass-balance conditions. For $v > v_{eq}$ the mass-balance equations are more complicated (*cf.* Gran's second method below).

Since the use of straight-line regression would no doubt improve the precision of the evaluation, a $\Delta v/\Delta E$ plot would appear to be preferable to a $\Delta E/\Delta v$ plot. It ought, however, to be stressed that even small errors in e.m.f. readings cause great deviations of the $\Delta v/\Delta E$ plot from linearity. This is illustrated in Fig. 3 by the two dashed extreme curves $1/(\Delta E \pm 0.1)$ encompassing the $\Delta v/\Delta E$ plot.

The Liteanu–Cörmös[15] *method.* This method is similar to Gran's method in that $\Delta v/\Delta E$ values are used. However, instead of plotting the $\Delta v/\Delta E$ values against $(v_n + v_{n+1})/2$, a correction for the difference in slope at $v = v_n$ and $v = v_{n+1}$ is applied. Moreover, the best straight lines before and after the end-point are calculated, instead of being evaluated graphically, using the statistical formula for straight-line regression. For asymmetrical titration curves, an asymmetry coefficient is obtained during the regression calculations.

The values obtained for v_{end} are strongly dependent on the Δv value chosen as is obvious from the results:

Volume interval	Δv	v_{end}
1–35 ml	1	24.8
10–35 ml	0.5	25.5

The Cavanagh[16]*–Herringshaw*[17] *method.* The aim of this method, which is also partly based on mass-balance conditions, is to predict the v value of the end-point from titration data obtained at the beginning of the titration. From two successive titration points, v_n and v_{n+1}, the end-point is predicted according to

$$(v_{end} - (v_n + v_{n+1})/2)^{-1} = F\Delta E(RT\Delta v)^{-1} - (v_0 + (v_n + v_{n+1})/2)^{-1}$$

where F, R and T have their usual physical meanings.

When this formula was applied to the first five 1-ml increments, the following end-point values were obtained: 24.90, 25.15, 25.00, 25.18 and 25.05 ml. The mean value, 25.06 ml, is close to the theoretical equivalence value, but, on the other hand, the precision of the prediction is only *ca.* ± 1 ml if e.m.f. errors are taken into account.

METHODS BASED ON MASS-BALANCE AND EQUILIBRIUM EQUATIONS

Titration to a pre-selected e.m.f. value

In this method, which is frequently applied in automatic titrators, the e.m.f. value in the equivalence point has either been previously determined experimentally or predicted by calculation. The e.m.f. value can, for instance, be calculated from the pF value at $v = 25$ ml in the titration curve shown in Fig. 1 provided that a relevant E° value is known for the electrode couple. In theory, it should thus be possible to determine v_{eq} very accurately but in practice electrode potential reproducibility puts a limit on the possible precision.

Gran's second method[18]. *The Ingman–Still extension*[19,20]

This method is based on the assumption that in all titration curves of analytical interest there is always a predominant main reaction. In this example, for instance, the reaction.

$$Th^{4+} + 4F^- \rightleftharpoons ThF_4(s)$$

predominates for $v < v_{eq}$ (*cf.* Fig. 1). Thus, the amount of free fluoride ought to decrease in proportion to the amount of thorium added, *i.e.*

$$[F^-] \propto (v_{eq} - v)/(100 + v)$$

By plotting $F_1 \propto (100+v)\,[F^-]$ against v ml, a straight line is, thus, obtained which, when extrapolated to $F_1 = 0$, intersects the v axis at $v = v_{eq}$. A value proportional to $[F^-]$ can, of course, be obtained from the Nernst relation without its being necessary to know the relevant $E°$ value for the electrode couple. The plot F_1 is shown in Fig. 4, and since the deviations from F_1 caused by e.m.f. errors are extremely small, it has not been possible to indicate them in the Fig. The intersection of F_1 on the v axis corresponds to an equivalence volume of 25.0 ml.

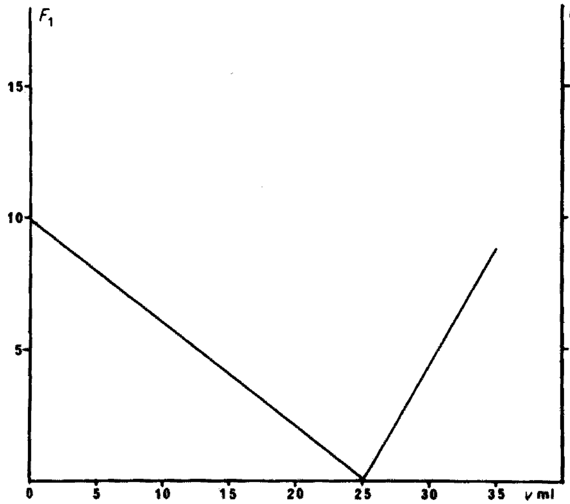

Fig. 4. Gran plots $F_1 = (100+v)[F^-]$ ($v < 25$ ml) and $F_2 = (100+v)[F^-]^{-2}$ ($v > 25$ ml) for the titration of 100 ml of 0.001 M sodium fluoride with v ml of 0.001 M thorium nitrate. The curves are plotted on an arbitrary scale.

From the computer calculations it can, furthermore, be seen that for $v > v_{eq}$ the amount of ThF_2^{2+} formed is proportional to the amount of excess thorium added (*cf.* ref. 21, Fig. 2), *i.e.*

$$(100+v)[ThF_2^{2+}] \propto (v - v_{eq}) \qquad (v > v_{eq})$$

which by introducing the solubility product for ThF_4 and the stability constant for ThF_2^{2+}, can be rewritten as

$$(100+v)[F^-]^{-2} \propto (v - v_{eq})$$

Thus, by plotting $F_2 \propto (100+v)[F^-]^{-2}$ against v ml, a straight line is obtained, which, when extrapolated to zero, intersects the v axis at $v=25.0$ ml, as shown in Fig. 4.

As pointed out above, Gran's second method can only be applied if there is a dominant main reaction. In a rigorous treatment the validity of the Gran plots ought to be checked by, for example, HALTAFALL calculations[22,23].

In the Ingman–Still extension[19] of Gran's method corrections are made for a competing side-reaction. Assume, for instance, that the fluoride solution had been made acidic so that the reaction

$$Th^{4+} + 4\,HF \rightleftharpoons ThF_4(s) + 4\,H^+$$

competed seriously with the main reaction

$$Th^{4+} + 4\,F^- \rightleftharpoons ThF_4(s)$$

Then, according to the mass-balance equations, the total amount of fluoride would decrease in proportion to the amount of thorium added, *i.e.*

$$(100+v)([F^-]+[HF]) \propto (v_{eq}-v)$$

which can be rewritten as

$$F'_1 \propto (100+v)(1+\beta_{HF}[H^+])[F^-] \propto (v_{eq}-v)$$

Thus, by plotting F'_1 against v ml, a straight line will be obtained which, when extrapolated to zero, intersects the v axis at $v=v_{eq}$.

It must, however, be emphasized that in order to be able to apply the Ingman–Still extension of Gran's method to this example, a fairly accurate value of β_{HF} must be known, and, moreover, the pH must be measured during the titration.

Multi-parameter refinement methods

The form of the E mV *vs.* v ml titrant curve in this example is governed by the following parameters

$$E = f([H]_{tot}, [F]_{tot}, v, t, E^\circ, \beta_{ThF}, \beta_{ThF_2}, \beta_{ThF_3}, \beta_{Th(OH)_2}, \beta_{Th_2OH},$$
$$\beta_{Th_2(OH)_2}, \beta_{Th_2(OH)_3}, \beta_{Th_6(OH)_{14}}, \beta_{Th_6(OH)_{15}}, K_{s0}, \beta_{HF}, \beta_{HF_2}, K_W)$$

where the function f can be expressed arithmetically by means of mass-balance and equilibrium equations. It is thus possible, by means of a computer, to generate sets of theoretical E *vs.* v curves. By varying all parameters according to a suitable strategy, a best fit between experimental and calculated curves is obtained from which $[F]_{tot}$ can then be evaluated. Such calculations are, of course, very complicated and, moreover, the number of experimental points must exceed the number of parameters in order to achieve statistical significance. On the other hand, some of the parameters, such as the stability constants for all acid–base reactions, contribute only slightly to the form of the titration curve (*cf.* Fig. 1). These constants can thus be kept constant at their approximate values during the refinement process. Moreover, some parameters are known accurately, *e.g.* v, $t=0.001$, $[H]_{tot}=0$, which further reduces the number of parameters to be varied. These parameters are then $[F]_{tot}$, E°, the stability constants β for ThF and ThF_2 and the solubility product K_{s0} for ThF_4. The accuracy and precision obtained in a multiparameter refinement method would be expected to be extremely high.

Even though there are several computer programs available[24-41] which are capable of carrying out multi-parameter refinements it seems likely that it may take some time before this method of evaluation comes into common analytical usage.

CONCLUSIONS

It has been shown that by considering the accurately calculated titration curve, it is possible to select the optimal end-point evaluation method for a specific titration with regard to systematic error, precision and time needed for a single end-point determination. Such a titration curve, moreover, rules out the necessity for the numerous approximate formulae for the estimation of titration errors (*cf.* ref. 1, Table I).

Although the discussions have been confined to a single example, it is probably safe to conclude that from the point of view of systematic errors decreasing error is obtained by: methods based on sigmoid curves > differential methods based on $\Delta E/\Delta v$ plots > differential methods based on $\Delta v/\Delta E$ plots > methods based strictly on mass-balance and equilibrium equations. This is also the approximate order of increasing precision. For very simple reactions with symmetrical titration curves, such as the titration of hydrochloric acid with sodium hydroxide, the approximate order of increasing precision is that given above, while systematic errors are of minor importance.

These results should be of interest, especially in the construction of automatic titrators and of computer programs for the evaluation of equivalence points from titration data.

The authors wish to express their gratitude to Prof. David Dyrssen, Head of the Department, for valuable discussions. A grant from Knut and Alice Wallenbergs Stiftelse to cover the cost of the Hewlett-Packard 2114B computer is also gratefully acknowledged. This work has been supported by the Swedish Natural Science Research Council. The English text of this paper has been revised by Dr. Susan Jagner.

SUMMARY

Accurately calculated titration curves make it possible to select the optimal method for evaluating the end-point of a particular potentiometric titration, with respect to systematic error, precision and time required. The potentiometric titration of fluoride with thorium(IV) solution is used as an example. Decreasing systematic error is obtained by the different methods in the following order: methods based on sigmoid curves > differential methods based on $\Delta E/\Delta v$ plots > differential methods based on $\Delta v/\Delta E$ plots > methods based on mass-balance and equilibrium equations. Increasing precision is obtained in approximately the same order. The conclusions appear to be generally applicable and are useful in the construction of automatic titrators.

RÉSUMÉ

Des courbes de titrage, calculées avec précision, permettent de choisir la méthode optimale pour l'évaluation du point final d'un titrage potentiométrique particulier, en fonction de l'erreur systématique, de la précision et du temps nécessaire. On donne comme exemple le titrage potentiométrique des fluorures au moyen de thorium(IV). Les conclusions sont généralement applicables et sont utiles pour la construction de titreurs automatiques.

ZUSAMMENFASSUNG

Genau berechnete Titrationskurven ermöglichen die Auswahl der optimalen Methode zur Ermittlung des Endpunktes einer einzelnen potentiometrischen Titration im Hinblick auf systematische Fehler, Reproduzierbarkeit und Zeitaufwand. Als Beispiel wird die potentiometrische Titration von Fluorid mit Thorium(IV)-Lösung behandelt. Es werden nach den verschiedenen Methoden abnehmende systematische Fehler in folgender Reihenfolge erhalten: auf S-Kurven beruhende Methoden > Differentialmethoden mit $\Delta E/\Delta v$-Auftragung > Differentialmethoden mit $\Delta v/\Delta E$-Auftragung > Methoden, die auf Mengenbilanz- und Gleichgewichtsgleichungen beruhen. In annähernd derselben Reihenfolge nimmt die Reproduzierbarkeit zu. Die Folgerungen scheinen allgemeingültig zu sein und sind für die Konstruktion automatischer Titratoren von Nutzen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A COMPUTER-PROCESSED SEMI-AUTOMATIC TITRATOR FOR HIGH-PRECISION ANALYSIS

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(Received 27th May 1971)

Increasing access to computers in the analytical laboratory has altered the design of automatic titrators. Since it is possible to process rapidly a large amount of titration data with a computer, automatic titrators can now be constructed to produce, in digitalized form, a wealth of data from a single titration. These data should be rendered in a form which makes them easy to feed into the computer, *e.g.* on punched tape. Automatic titrators based on these principles have been described for example, by Johansson and Pehrsson[1] and by Jagner[2], and similar equipment is now available commercially[3,4]. In the titrator described by Jagner[2] it is, for instance, possible to pre-set the magnitude of the increment of titrant, and the time interval between two successive additions, and it is also possible to discriminate sensor signals below a pre-chosen magnitude from being printed out on punched tape. Even though these programming facilities are, no doubt, satisfactory for many titration purposes, they are by no means sufficient if a particular procedure is to be optimized with respect to precision and time required for a single analysis. Increased programming facilities can, of course, be obtained by adding different relay functions to the titrator. However, in view of the tremendous power inherent for processing purposes in the modern mini-computers now available, the coupling of such a computer to the titrator seemed, however, to be the logical way of increasing its capacity.

In this paper the computerized version of the semi-automatic titrator described previously[2] is presented. The system has been designed to meet the requirements set both by the research laboratory and by the routine laboratory. For research purposes great emphasis has been placed on making the computer as easy as possible to program. In this way it should be feasible to optimize many different titration procedures without allowing programming difficulties to overshadow the chemical problems involved. For the purposes of routine analysis the titrator has been equipped with a large number of in- and output channels so that, once the optimum titration procedure has been developed, several analyses may be run in parallel.

DESCRIPTION OF THE TITRATOR

A schematic diagram of the titrator is given in Fig. 1 and the different components are discussed below. Some of the components have been described previously[2] in more detail.

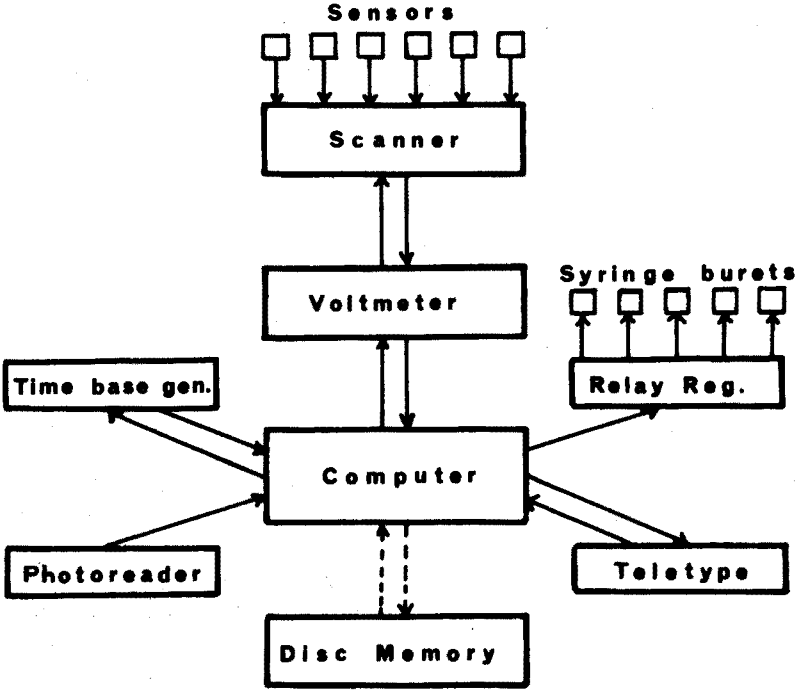

Fig. 1. Block diagram of the titrator. The maximum possible number of sensors and syringe burets is 100 and 16, respectively.

Computer

The computer is a Hewlett-Packard HP 2114 B equipped with a core memory of 8192 words, the word-length being 16 bits. The computer is prepared for direct memory access (DMA) to, for example, a disc memory.

Time base generator

The time base generator, HP 12539 A, makes it possible to register the time which has elapsed after the commencement of the process initiating the generator. The generator can operate at seven different pre-chosen time intervals, namely 100 μsec, 1 msec, ... 1000 sec, *i.e.* when operating at the lowest time interval, the value of the generator is increased by one unit every 100 μsec. Since the value generated by the time base generator is stored in one 16-bit word, the maximum total time which it is possible to store will be $2^{15} \times$ the time interval. When the generator is operated at the 100-μsec time interval, the process under study must be completed within 3.3 sec, while the corresponding value for the 1000-sec interval is 380 days.

Teletype

The teletype is an ASR 33 modified for on-line operation with the computer. The maximum speed for printing out results is *ca.* 10 characters $\sec^{-1}$. Since the teletype is equipped with a transmitter unit it would be possible to transfer experimental data, which need time-consuming computation (*e.g.* multiparameter refinements), to a larger computer.

Photoreader

The photoreader, HP 2737 A, can read punched tape at a maximum speed of 500 characters sec^{-1}.

Voltmeter

The voltmeter (Dynamco DM 2006) is an integrating digital voltmeter which can register to four significant figures in four different measuring ranges, *viz.* 0–100 mV, 0–1 V, 0–10 V and 0–100 V. The voltmeter is equipped with an automatic ranging function (Dynamco Input Module D3) and has an input impedance of *ca.* 10000 MΩ. An input filter with a time-constant of about 100 msec can be connected to the voltmeter input. In one measuring cycle the voltmeter uses 20 msec for integrating, a maximum of 20 msec for measuring the time needed for discharging, and 10 msec for the stabilizing period. This means that a maximum of 20 voltmeter readings sec^{-1} can be fed into the core memory of the computer. This is, of course, a very low speed on a computer time scale, but it is more than sufficient for most titration analyses. The voltmeter is interfaced to the computer via standard hardware equipment, HP 12604 B, the voltmeter information stored in computer memory being signal sign, four figures and position of decimal point.

Scanner

The analogue signals to be measured in a titration procedure enter the digital voltmeter via a scanner. This consists of ten modules, each module having ten input channels (Dynamco, Low Level Scanners DS 6001), the input impedance being 10000 MΩ. This means that analogue signals from 100 different sources can be measured in the same analytical procedure. The scanner is processed by the computer using two interface cards, HP 12566A-01, according to the driver routines outlined below.

Relay register

The 16-bit relay register, HP 12551 B, processes the syringe burets of the titrator by a direct delivery of short-circuiting pulses of programmable duration to the buret motors. Since one buret can be connected to each relay bit, 16 burets can be operated simultaneously and independently of each other. The register can, of course, be used to operate equipment other than burets.

Syringe burets

All syringe burets used hitherto in the titrator have been Metrohm Dosimat E 415 with total volumes of 10 or 20 ml. The buret readings can be recorded by the computer in two different ways. The motor axles of the syringe burets are coupled to potentiometers which yield voltages, in the range 0–1 V, proportional to the total volume of titrant added. Since, however, these potentiometers must be calibrated frequently, it is often simpler to operate the burets in “increment addition” position. In this position a relay pulse of approximately 200 msec duration causes the buret to release a single increment. The magnitude of this increment is 0.05 ml if the total buret volume is 10 ml and 0.1 ml if the total volume is 20 ml. The number of pulses generated, which will be proportional to the total volume of titrant added, is summed by the computer.

Sensors

Any equipment which delivers analogue voltage signals in the range 0–100 V can be used as a sensor. Apart from electrodes and photometers, which are the equipment most frequently used in titration procedures, many instruments in use in the analytical laboratory can therefore function as sensors. The "titrator" can thus be used for analytical purposes other than titrations. When sensors with high output impedances, *e.g.* glass electrodes, are used, a high quality operational amplifier must be inserted as a voltage follower before the signal enters the input channel.

PROGRAMMING THE TITRATOR

The programming facilities are of fundamental importance for the versatility of the titrator. The computer has compilers for three different language levels namely Assembler, Fortran and Algol, and Basic, which are all described in detail in the manufacturers' manuals.

Assembler

Apart from machine code itself, Assembler is the language which is most intimately connected with the electronic logics involved in the operation of the computer. It is therefore also the most difficult to use for programming purposes. The language must, however, be used for the construction of driver routine programs, *i.e.* programs which process input and output from different peripheral equipment such as photoreader, scanner and voltmeter. The peripheral equipment normally operates at a much lower speed than the computer. The maximum speed at which a specific equipment is able to operate when electronically interfaced with the computer must be determined before appropriate driver routines can be constructed. In the driver routine programs for the scanner, delay times of 20 msec have been included in order to allow time for relay bounces to subside. Thus, taking into account the 50 msec required by the voltmeter for one measuring cycle, the maximum number of readings $\sec^{-1}$ will be *ca.* 15. If, however, the voltmeter filter is used, a delay time of at least 1 sec must be included between the opening of the appropriate channel and the commencement of readings at the maximum rate.

As mentioned earlier, the peripheral equipment operates at a much lower speed than the computer. The driver routine programs can, however, be constructed so that they make use of the interrupt functions of the computer. When interrupt drivers are used, the command returns to the main computer program after the specific peripheral has been initiated, *i.e.* after the trip signal from the computer reaches the digital voltmeter. The computer can then perform, for example, calculations until the voltmeter has finished sampling. On titration time scale, interrupt drivers normally offer only small advantages over non-interrupt drivers.

Algol and Fortran

The computer has compilers for Algol and Fortran. The latter takes up 8 K words in the memory and must therefore be fed into the computer in two passes.

Basic

Since Basic is a dialogue language the compiler must be stored in the core memory both during programming and during the execution of a program. The advanced HP Basic compiler takes up 5.8 K words of the core memory, but this can be reduced to 4.7 K words if the matrix operations are removed. All peripheral equipment can be operated on the Basic language level using special "Basic CALL statements" exemplified in Table I. This considerably simplifies the construction and optimization of titration procedures.

TABLE I

EXAMPLES OF BASIC CALLABLE DRIVER ROUTINES

Statement no.	*Statement*	*Comment*
2000	CALL (1, 2)	Start time generator on range 1 msec
2005	LET I=0	Give the variables I and
2010	LET A=0	A the initial value zero
2020	FOR K=1 TO 10	Repeat statements 2020–2070 ten times
2030	CALL (6, 3)	Open scanner module No. 3
2040	CALL (7, 7)	Open channel No. 7 in module No. 3
2050	CALL (8, V)	Read the value of V from the voltmeter
2060	LET A=A+V	Increase the value of A by V
2070	NEXT K	Return to 2030 if K < 10
2090	LET I=I+1	Increase the value of I by one unit
2100	LET E(I)=A/10	Calculate average e.m.f. value
2110	IF I<1.5 THEN 2010	Return to 2010 if I<1.5
2120	IF ABS(E(I)–E(I–1)) >.01 THEN 2010	Return to 2010 if the absolute value of two consecutive sets of readings >0.01
2130	CALL (2, R)	Read time generator value, R
2135	FOR Q=1 TO 3	Repeat statements 2135–2165 three times
2140	CALL (3, 10)	Open relay to buret No. 10
2150	WAIT (250)	Wait 250 msec for one titrant increment
2160	CALL (4, 10)	Close relay to buret No. 10
2165	NEXT Q	Return to 2140 if Q < 3
2170	RETURN	Return to main program

Example of the use of Basic callable driver routines

Since Basic callable driver routines form an essential part of the principle of the titrator, their use is illustrated in an example given in Table I. In this example, which is assumed to form part of a larger program, 10 e.m.f. readings (V) are registered, after which their average value (E[I]) is calculated. A new set of 10 e.m.f. readings is then registered and a new average value calculated. This is repeated until two consecutive average values differ by less than 0.01 units. Using the time base generator, the computer then registers the time passed from the commencement of the registering of the e.m.f. values until the requirement has been fulfilled. Finally, the program causes a buret to make three titrant increments and then returns to the main program.

Since the compiler is stored in the core memory during programming and execution it is very easy to change a statement in a program. If, for instance, the number of titrant increments in the example in Table I is to be changed from three to five it is only necessary to type

```
2135 FOR Q = 1 TO 5
```

on the teletype keybord. Since a large number of such changes can be made very rapidly, it is easy to test several different approaches. This is a vital factor in the optimization of a specific titration procedure.

Comparison between different language levels

The main difference between the three language levels lies in the time needed to construct a specific program and the time required by the computer to execute the program. As a rough estimate it may be said that programming in Basic is ten times more rapid than programming in Fortran which, in its turn, is ten times more rapid than Assembler. If the computer is equipped with a disc memory in which the Fortran compiler can be stored, the difference in rapidity between Basic and Fortran is considerably less. The opposite, with the same orders of magnitude, is true for execution time, Assembler being the fastest and Basic the slowest. The simplicity of programming in Basic is counter-balanced by the limited amount of core memory (= 3.3 K) available for computer programs and experimental data. Once an optimal titration procedure has been developed it is therefore advantageous to translate the program into Fortran. This, besides decreasing the execution time, also decreases the amount of core memory space required for the storage of the program, and thus makes it easier to run several programs in parallel.

OTHER USES OF THE SYSTEM

Since the voltmeter can handle analogue signals in the 0–100 V range, it can register the output signals of a great number of analytical instruments. The system can, for instance, be used for spectra recording, gas chromatographic analysis and atomic absorption spectroscopy. The computer itself provides, of course, great facilities for ordinary computational work.

The authors would like to express their sincere gratitude to the head of the Department, Professor David Dyrssen, for valuable discussions. Grants from Knut and Alice Wallenbergs Stiftelse to cover the cost of the computer and from Carl Tryggers Stiftelse to cover the cost of the titrator are gratefully acknowledged. The titrator has been interfaced to the computer by B.G. Wingren and W. Vateman, Datametrix AB., Sweden. This work forms part of a larger project on the analytical chemistry of sea water, supported financially by the Swedish Natural Science Research Council.

SUMMARY

A mini-computer processed semi-automatic titrator equipped with an analogue scanner, a digital voltmeter and a 16-bit relay register is described. The scanner has 100 channels available for input voltages and the voltmeter can measure signals in the range 0–100 V at a maximum rate of 20 readings sec^{-1}. The relay register can be used to process simultaneously a maximum of 16 motor-driven syringe burets independently of each other. The titrator can be programmed in Assembler, Fortran and Basic. A major principle behind the design of the titrator is simplicity in programming,

and this is achieved by the use of Basic callable subroutines to all peripheral equipment *e.g.* scanner, voltmeter and relay register. The titrator is therefore especially suitable for use in the research analytical laboratory.

RÉSUMÉ

Un titreur semi-automatique à mini-ordinateur, équipé avec "scanner", voltmètre digital et enregistreur est décrit. Cet appareil convient tout spécialement à un laboratoire de chimie analytique, en recherches.

ZUSAMMENFASSUNG

Es wird ein halbautomatischer Titrator beschrieben, der mit einem Kleinstrechner gesteuert wird und mit einem Analogabtaster, einem Digitalvoltmeter und einem 16 bit-Relaisregister ausgerüstet ist. Der Abtaster verfügt über 100 Kanäle für Eingangsspannungen, und das Voltmeter kann Signale im Bereich 0–100 V mit einer maximalen Lesegeschwindigkeit von 20 Zeichen sec^{-1} messen. Mit dem Relaisregister können unabhängig voneinander maximal 16 Motor-Kolbenbüretten simultan gesteuert werden. Der Titrator kann in Assembler, Fortran und Basic programmiert werden. Ein wesentliches Prinzip neben der Titratorkonstruktion ist Einfachheit der Programmierung. Sie wird durch die Anwendung von in Basic aufrufbaren Unterprogrammen für alle peripheren Geräte wie Abtaster, Voltmeter und Relaisregister erreicht. Der Titrator eignet sich deshalb besonders für die Verwendung in analytischen Forschungslaboratorien.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A COMPUTER-PROCESSED HIGH-PRECISION COMPLEXIMETRIC TITRATION FOR THE DETERMINATION OF THE TOTAL ALKALINE EARTH METAL CONCENTRATION IN SEA WATER

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(Received 27th May 1971)

Sea water of 35‰ salinity is approximately 0.05 *M* in magnesium, 0.01 *M* in calcium and 0.0001 *M* in strontium, other divalent metals being present at the p.p.b. level. In procedures for determining the individual concentrations of magnesium and calcium, one of these constituents is usually determined separately. The concentration of the other is then derived from the total concentration of alkaline earth metals obtained by titration with EDTA[1], the strontium concentration having also been determined separately by means of atomic absorption or flame emission spectroscopy. The precision of the calcium and magnesium determinations are thus dependent on the precision of the determination of the total concentration of alkaline earth metals. In this paper a high-precision computer-processed titration procedure for the photometric determination of the total alkaline earth metal concentration, with EDTA and eriochrome black T, is described.

THEORY

In a photometric indicator titration procedure, the titration conditions must usually be adjusted so that a break-point is obtained on the titration curve[2]. In the case of the titration of sea water with EDTA, with eriochrome black T as indicator, this is best achieved by means of a high pH in the titration vessel. The maximum pH possible is governed by the precipitation of magnesium hydroxide which occurs at pH values above 10.5 in dilute sea water.

In order to determine the optimal method for evaluation of the photometric titration data, a theoretical titration curve was calculated by means of the computer program HALTAFALL[3,4]. The calculations were performed as a titration of 180 ml of 0.008 *M* magnesium with v ml of 0.1 *M* EDTA at pH 10.5. The total concentration of eriochrome black T was $3 \cdot 10^{-6}$ *M* and the calculations were performed with an accuracy[3,4] of 0.005% of the total concentrations of magnesium, EDTA and indicator. The stability constants used in the calculations are those specified in Table I. Calcium was not included as a component since it does not contribute to the form of the titration curve in the vicinity of the equivalence point, owing to the formation of strong EDTA but weak indicator complexes[4]. Nor, owing to its very low concentration, does strontium contribute significantly to the form of the titration curve.

The computer results, which are illustrated in Fig. 1, indicate two possible

TABLE I

STABILITY CONSTANTS USED IN THE COMPUTER CALCULATION OF THE THEORETICAL TITRATION CURVE SHOWN IN FIG. 1
(H_4Y denotes EDTA and H_3I denotes eriochrome black T)

Reaction	*Log. of stability constant*
$Mg^{2+} + Y^{4-} \rightleftharpoons MgY^{2-}$	8.70
$H^+ + Y^{4-} \rightleftharpoons HY^{3-}$	10.34
$2\,H^+ + Y^{4-} \rightleftharpoons H_2Y^{2-}$	16.58
$Mg^{2+} + I^{3-} \rightleftharpoons MgI^-$	7.18
$H^+ + I^{3-} \rightleftharpoons HI^{2-}$	11.60
$2\,H^+ + I^{3-} \rightleftharpoons H_2I^-$	17.90

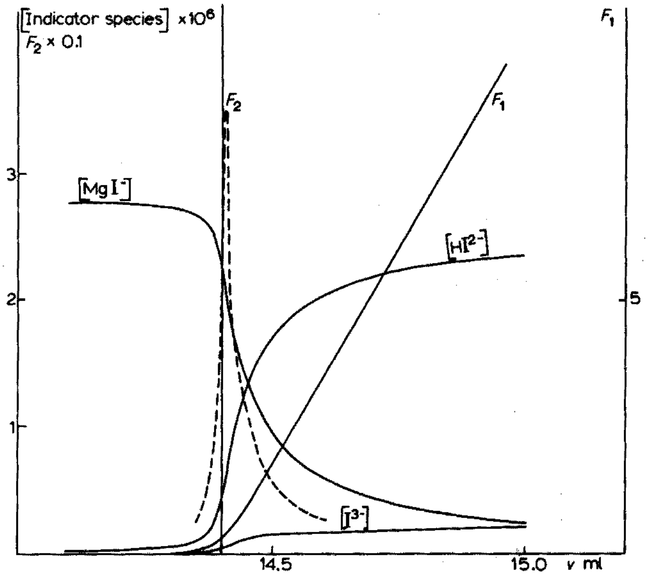

Fig. 1. Results from the computer calculations of the theoretical titration curve. $F_1 = [HI^{2-}]/[MgI^-]$, $F_2 = \Delta[HI^{2-}]/\Delta v$ (Δv 0.005 or 0.01 ml). The vertical line at 14.40 ml represents the theoretical equivalence point.

ways of evaluating the equivalence point from photometric titration data. In the first method, which is similar to Gran's[5] treatment of potentiometric titration data, it is assumed that no metal–EDTA complexes are formed by the excess of EDTA added after the equivalence point, v_{eq}. If this assumption is correct it can be shown that

$$[Mg^{2+}]^{-1} \propto v - v_{eq} \qquad (v > v_{eq}) \tag{1}$$

Since at constant pH the ratio

$$[MgI^-][Mg^{2+}]^{-1}[HI^{2-}]^{-1} \tag{2}$$

is constant, the plot F_1, where

$$F_1 = [HI^{2-}][MgI^-]^{-1} \propto v - v_{eq} \tag{3}$$

against v ml of titrant added will be linear and should, moreover, when extrapolated to $F_1=0$, intersect the v-axis at $v=v_{eq}$. The ratio $[HI^{2-}][MgI^-]^{-1}$ can be derived from photometric absorbance data according to procedures outlined by Higuchi *et al.*[6], Still and Skrifvars[7] and Dyrssen *et al.*[4]. As is seen from Fig. 1, the plot of F_1 against v ml is linear for $v > 14.50$ ml and, if the linear part is extrapolated to zero, it intersects the v-axis at the theoretical equivalence point, 14.40 ml.

The second evaluation method indicated by Fig. 1 involves the location of the inflexion point on the titration curve (absorbance *versus* v ml). This is equivalent to finding the maximum of the plot $F_2=\Delta[HI^{2-}](\Delta v)^{-1}$ against v ml as shown in Fig. 1 (Δv here is 0.005 or 0.01 ml). As is seen from this plot, a maximum change in absorbance occurs at $v \sim 14.41$ ml close to the theoretical equivalence point, the values of the ratio $[HI^{2-}][MgI^-]^{-1}$ in the inflexion and equivalence points being approximately 1 : 3. Moreover, it can be observed that the plots $[HI^{2-}]$ and $[MgI^-]$ are nearly linear in the region of the inflexion and equivalence points. Thus, by obtaining sufficient titration data (absorbance *vs.* ml EDTA) in the region of the inflexion point and fitting the best straight line through these data, it ought to be possible to determine a point close to the inflexion and equivalence points with high precision. The absorbance corresponding to this point, A_{pr}, is given by

$$A_{pr} = 0.75\,A_{min} + 0.25\,A_{max} \tag{4}$$

where A_{max} (approx. $\propto [HI^{2-}]$) is the absorbance value for $v \gg v_{eq}$ and A_{min} (approx. $\propto [MgI^-]$) is the absorbance value for $v \ll v_{eq}$.

Since this evaluation method only approximately locates the true equivalence point, it is necessary to standardize the procedure against solutions containing known concentrations of magnesium and calcium buffered to the same pH value as the sea-water samples. Both evaluation methods mentioned above have been tested in practice. In spite of the fact that the F_1 method is more satisfactory theoretically, the inflexion point method has been found to give, in practice, results of higher precision. This is mainly due to the fact that the F_1 method requires more accurately determined absorbance data than the inflexion point method. A photometer with a selenium photocell of the type used in the titrations is, however, seldom capable of giving accurate absorbance readings over a high concentration range. Although the use of a spectrophotometer would undoubtedly favour F_1 evaluation, in such a method the titration vessel would have to be protected from indirect light so that only light from the spectrophotometer beam reached the detector. Since this would make the whole titration procedure much more difficult to carry out, it was decided to retain the photometer and to use the inflexion point method to evaluate the titration data.

EXPERIMENTAL

Apparatus

The titrations were performed with the computer-processed titrator described by Anfält and Jagner[8]. An EEL Quantitrator photometer (Evans Electroselenium Ltd, Halstead, England) with an Ilford narrow band filter (No. 607; peak wavelength of 600 nm) was used. The current output from the selenium photocell was led through a load resistance of 1500 Ω and the voltage drop was registered to four significant figures in the 0–100 mV range by the digital voltmeter of the titrator.

The syringe burets used were Metrohm Dosimat E 415 with a total volume of either 10 or 20 ml. The buret tips, which were allowed to dip into the titration vessel, were made from 5-cm capillaries with an inner diameter of 0.6 mm.

Reagents

Synthetic sea-water solutions. These were prepared with the approximate composition 0.053 M_w magnesium, 0.01 M_w calcium ($CaCO_3$ p.a. Merck AG), 0.0001 M_w strontium ($SrCl_2(H_2O)_6$ p.a. Riedel-De Haen AG), 0.56 M_w sodium chloride (p.a. Merck AG) and 0.028 M_w sodium sulphate (p.a. Merck AG), where M_w denotes moles per 1000 g of solution. Three different magnesium standards were used, *i.e.* spectrographic-grade magnesium ribbons (B.D.H.), spectrographic-grade magnesium turnings (B.D.H.) and spectrographic-grade magnesium ingots (Koch-Light). The magnesium ribbons and ingots were first carefully polished to remove adhering oxide and then washed with ethanol. The magnesium metal samples were dissolved, together with the calcium carbonate, in a stoichiometric amount of dilute hydrochloric acid.

Dilute synthetic sea-water solutions. These were prepared by diluting weighed amounts of synthetic sea water into weight-calibrated volumetric flasks so that the total alkaline earth metal concentration was approximately 0.01 *M*.

EDTA solutions (P.H. Tamm, Altuna, Sweden). These solutions were prepared from the disodium salt so as to be *ca.* 0.1 *M* and sodium hydroxide was added to achieve the stoichiometric composition of the tetrasodium salt.

Buffer solution. Buffer was prepared by dissolving 95.4 g of borax (May and Baker) and 18.2 g of sodium hydroxide (p.a., EKA, Sweden) in doubly distilled water and diluting to 1 l.

Eriochrome black T (Kebo, Sweden). The solution was made 0.003 *M* in 95% ethanol.

Standard sea water of $35^0/_{00}$ *salinity* $(19.3745^0/_{00}$ *chlorinity).* Purchased from I.A.P.S.O., Standard Sea Water Service, Charlottenlund Slot, Denmark.

Doubly distilled water from the same still was used in the preparation of all standard solutions and for the dilution of all sea-water and standard samples.

Preparation of the samples.

The amount of sea water, which must be accurately weighed into the titration vessel, should be chosen so that the total magnesium concentration in the titration vessel is always of the same order of magnitude. For a sea-water sample with a salinity of $S\ ^0/_{00}$ the weight of the sample should, for the titration procedure outlined below, be chosen so that

$$\text{weight sample} \cdot S \sim 900 \tag{5}$$

i.e. for sea water of $35^0/_{00}$ salinity, samples of approximately 25 g should be weighed in.

The samples are then diluted with doubly distilled water to a total volume of 180 ml, after which 2 ml of indicator and 20 ml of buffer solution are added.

Computer-processed titration procedure

The computer-processing program for the titrator was written in Basic and only the main features of the program are outlined here. A copy of the program may be obtained on request from the authors. After the preparation of the sample the input data, *viz.* sample number, sample weight, photometer reading before addition of indicator (for the absorbance calculations) and temperature in the EDTA storage vessel, are fed into the computer through the teletype input. The temperature reading is used by the titrator to compensate for changes in the molarity of the EDTA solution caused by variations in room temperature. It was assumed in the program that the change in density of the EDTA solution with temperature is identical with that of pure water.

The titrator starts by adding 1.2-ml increments of 0.1 *M* EDTA and waits, after each increment, for a steady signal, according to the criterion described below. This procedure is continued as long as the absorbance value decreases (photocell signal increases) owing to dilution of the sample. When approximately 90% of the total volume of titrant needed for equivalence has been added, the value of the absorbance starts to increase, because of consumption of the magnesium–indicator complex. The titrator then begins to add 0.1-ml increments of EDTA and, at the same time, stores a value of $A_{\min}$ in the core memory. Addition of 0.1-ml increments is continued until the inflexion point has been passed. The criterion for having passed the inflexion point is that the last 0.1-ml increment of titrant yields a smaller change in absorbance than the preceding increment.

The titrator then starts back-titrating with 0.1-ml increments from a buret filled with dilute synthetic sea water (−0.01 *M* EDTA in the computer program). During the back-titration process the volume interval in which the inflexion point is passed is taken as being that increment which yields the greatest change in absorbance. The volume and absorbance values in the end-point of this increment are stored in the core memory. An 0.1-ml increment of EDTA is then added and a new inflexion point interval is found by the back-titration procedure. The back-titration procedure is repeated six times, by which time twelve volume, v_i, and twelve absorbance, A_i, values in the vicinity of the inflexion point have been stored in the core memory. Finally, the titrator adds a 1.5-ml increment of EDTA and registers $A_{\max}$. The volume changes during these additions are neglected, except in the calculation of $A_{\max}$.

During the evaluation process the computer starts by calculating the best straight line through the experimental v_i and A_i values. The equivalence point volume is then calculated as the volume corresponding to the absorbance, A_{pr}, defined as

$$A_{\mathrm{pr}} = 0.75\, A_{\min} + 0.25\, A_{\max} \tag{4}$$

Finally, the total alkaline earth metal concentration is calculated and the results are printed out on the teletype.

An example of experimental titration data in the vicinity of the inflexion point obtained in the titration of 25.36740 g of Standard Sea Water is shown in Fig. 2.

The criterion for a steady signal after each addition of titrant is the same for all points on the titration curve. As soon as the titrant increment has been added, the titrator registers twenty voltage readings within *ca.* 1 sec. The average value of the twenty readings is calculated and a new set of twenty readings is registered. This is continued until the average values of two consecutive sets of data differ by less than 0.15%. The average value of the last twenty readings is then taken to be the absorbance value in the specific titration point. Owing to the rapid attainment of equilibrium,

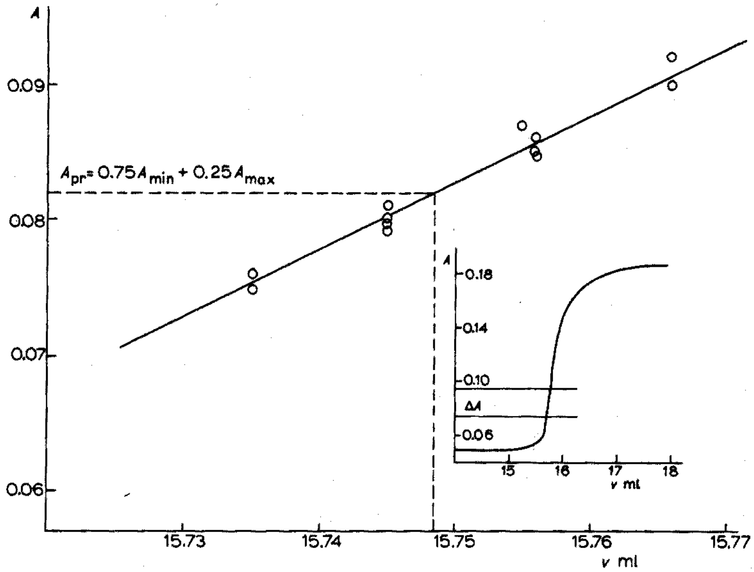

Fig. 2. An illustration of the evaluation of experimental absorbance and volume data in the inflexion point interval obtained in the titration of 25.36740 g of Standard Sea Water. A larger part of the titration curve is depicted to the right, the region denoted by ΔA being used for the calculation of A_{pr}.

the rapid response of the photocell and the vigorous stirring, a steady reading is often obtained a few seconds after the addition of titrant.

The time needed for one titration is about 15 min, which also includes the time needed for evaluating and printing the results.

RESULTS

The total concentration of alkaline earth metals in Standard Sea Water was determined with three different magnesium standards. In the determination, eight standardisations of EDTA against 25–28 g portions of the standard solution were followed by eight titrations of the same amount of Standard Sea Water. In order to test the reproducibility with which a specific standard could be prepared, two different

TABLE II

THE DETERMINATION OF THE TOTAL ALKALINE METAL CONCENTRATION, $[M^{2+}]_{tot}$, IN STANDARD SEA WATER
(The standard deviation is the mean value obtained in eight titrations of the standard solution and eight titrations of Standard Sea Water)

Standard reagent	$[M^{2+}]_{tot}$ in $35\,^0/_{00}$ *Standard Sea Water* (*mmole* kg^{-1})	*Standard deviation* (%)
Magnesium turnings(I)	63.715	0.009
Magnesium turnings(II)	63.719	0.010
Magnesium ribbons	63.314	0.011
Magnesium ingots	63.332	0.008

standards prepared from magnesium turnings were used. The results are shown in Table II. It is seen that the results obtained with magnesium turnings are rather high compared with those obtained with the two other magnesium standards. This is undoubtedly due to the presence of surface oxide.

The mean value obtained with magnesium ribbons and ingots, 63.32 moles per 1000 g of $35^0/_{00}$ sea water, is in good agreement with the mean value, 63.41, obtained for different North Atlantic samples by Riley and Tongudai[9].

DISCUSSION

Precision

As can be seen from the results given in Table II the titration method is associated with a high precision. This is achieved through the very large number of photocell and buret readings registered by the titrator during a single titration procedure. The precision-limiting factor in the titration procedure is probably provided by the volume errors associated with the syringe burets of which, of course, the EDTA buret is the most critical. Errors may also be introduced in the weighing-in process unless extreme care is exercized to avoid evaporation. The change in the response of the photocell with time has been investigated and has been found to play a minor role in the total precision of the titration procedure.

Accuracy

As is obvious from Table II, the accuracy of the method depends on the reliability of the reagents used to prepare the standard solutions. It is, of course, also dependent on the reproducibility with which a standard solution can be prepared from a specific reagent. That the pH values of the sea water and standard samples are the same is, of course, fundamental for the accuracy. In this work the titration curves obtained with the standards were identical in form with those obtained with the sea-water samples. As pointed out earlier, the magnesium and indicator concentrations in the titration vessel should always be of the same order of magnitude. Since there is a dilution step involved in the titration procedure, sea-water samples with salinities down to $5^0/_{00}$ can be covered by the method, provided that eqn. (5) is followed when sampling.

The amounts of metals in sea water complexing with EDTA, other than magnesium, calcium and strontium, are so small that their presence cannot significantly influence the accuracy of the method at the pH value employed in the titrations.

Significance to marine chemistry

As a consequence of evaporation, dilution and mixing processes, changes in the alkaline earth metal concentrations generally follow changes in chlorinity. Thus the ratio total moles of M^{2+} per kg of sea water : $^0/_{00}$ chlorinity ought to be practically constant. If, however, calcium carbonate is either formed by bioprocesses or dissolved by carbon dioxide, then these processes ought to be able to be detected by low or high total moles of M^{2+} per kg of sea water : $^0/_{00}$ chlorinity ratios, provided that the total alkaline earth metal concentration and the chlorinity[10] can be determined with high precision.

The authors would like to express their sincere gratitude to the head of the Department, Prof. David Dyrssen, for valuable discussions. Grants from Knut and Alice Wallenbergs Stiftelse and from Carl Tryggers Stiftelse to cover the cost of the computer-processed titrator are gratefully acknowledged. This work, like all other projects concerned with sea water performed at this Department, has been supported financially by the Swedish Natural Science Research Council.

SUMMARY

A computer-processed high-precision photometric titration procedure for the determination of the total alkaline earth metal concentration in sea water is described. Titrations are carried out at pH 10.5, with EDTA as complexing agent and eriochrome black T as indicator. The method yields a value of 63.32 mmoles per kg of $35^{0}/_{00}$ salinity for the total alkaline earth metal concentration in Standard Sea Water, and the precision of the method is *ca.* 0.01%.

RÉSUMÉ

On décrit un procédé de titrage photométrique à ordinateur, de haute précision, pour le dosage des métaux alcalino-terreux dans l'eau de mer. Le titrage se fait au pH 10.5, en utilisant l'EDTA comme complexant et le noir ériochrome T comme indicateur. La méthode fournit une valeur de 63.32 mmoles/kg à $35^{\circ}/_{\circ\circ}$ de salinité, pour la concentration totale en alcalino-terreux dans une eau de mer standard. La précision de la méthode est d'environ 0.01%.

ZUSAMMENFASSUNG

Für die Bestimmung der Gesamtkonzentration von Erdalkalimetallen in Meerwasser wird ein photometrisches Titrationsverfahren hoher Reproduzierbarkeit unter Anwendung eines elektronischen Rechners beschrieben. Die Titrationen werden bei pH 10.5 mit EDTA als Komplexierungsmittel und Eriochromschwarz T als Indikator ausgeführt. Die Methode ergibt für die Gesamterdalkalimetallkonzentration in Standard-Meerwasser von $35^{\circ}/_{\circ\circ}$ Salzgehalt den Wert 63.32 mmol/kg. Die Reproduzierbarkeit der Methode ist *ca.* 0.01%.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

CYCLOPENTANONE-2-CARBOXYANILIDE AS A REAGENT FOR THE GRAVIMETRIC, TITRIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM

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(Received 1st May 1971)

Various oxygen-containing organic reagents, including some 1,3-diketones, have been proposed for the gravimetric determination of beryllium in recent years[1-7] and the advantages of such reagents over phosphates, arsenates, etc. have been evaluated[8]. At least one reagent of this group[9] has also been used for the titrimetric determination of this metal by means of bromate solutions, while picolylketones[10,11] have been applied for both gravimetry and ultraviolet spectrophotometry. Many organic dyestuffs have been recommended for the colorimetric determination of beryllium, but extraction with acetylacetone[12] in the presence of disodium ethylenediaminetetraacetate followed by spectrophotometry is usually preferred owing to its greater selectivity. However, the absorption of the excess of reagent is a major disadvantage, and it is usually necessary to remove the unreacted reagent.

In the investigation described below, cyclopentanone-2-carboxyanilide, which contains an effective 1,3-diketo group, was found to be a reagent of exceptional merit for beryllium, even when compared to other members of the same class in use. As the solubility of the reagent is quite high, while that of the complex is low and the precipitate coagulates rapidly, the gravimetric procedure is simple. The complex may also be determined by titration with bromate, thus providing a titrimetric procedure for beryllium. Moreover, the complex is stable for days when extracted in isobutyl methyl ketone and beryllium can be determined conveniently by measuring the absorbance at 332 nm, as the reagent has no absorption at this wavelength.

The accuracies of these methods were found to be excellent when beryllium was determined alone, in a mineral like beryl, or in artificial mixtures containing appreciable quantities of various diverse ions masked with EDTA.

EXPERIMENTAL

Reagents and chemicals

Cyclopentanone-2-carboxyanilide. The reagent was prepared by the condensation of aniline with ethyl cyclopentanone-2-carboxylate[13]. This ester was obtained from adipic ester by Dieckman condensation.

For each determination of beryllium by the gravimetric or titrimetric method 0.4–0.5 g of the reagent was dissolved in 5 ml of aqueous ethanol or 10 ml of sodium hydroxide (1%) solution. For the spectrophotometric determinations the reagent was dissolved in the minimal amount of sodium hydroxide solution (2%), the excess of the alkali was neutralised with 2 *M* nitric acid, and the solution was diluted with water to a concentration of 5 mg of the reagent per millilitre.

Standard beryllium solution. Beryllium hydroxide was precipitated from a solution of beryllium nitrate in the presence of Na_2EDTA, washed, and dissolved in nitric acid. The solution was suitably diluted and standardized by the oxide method and by the N-benzoyl-N-phenylhydroxylamine method[1]. For the spectrophotometric studies, dilutions of this solution were used.

Diverse ions. Stock solutions were prepared from pure samples of nitrates, chlorides and sulphates of various metal ions. Sodium salts were used in the case of anions.

Standard solutions for titrimetric method. Stock solutions of 0.1 *N* potassium bromate and 0.1 *N* sodium thiosulphate were prepared.

Apparatus

A Cambridge pH-meter was used for the measurement of pH. Absorbances were measured with a Hilger-Watts H700 Uvispek spectrophotometer in 1-cm quartz cuvettes.

Procedure for gravimetric determination

Dilute the solution containing beryllium (1.4–4.0 mg) to about 100 ml, add 2 g of ammonium acetate and warm to 35–40°. Add the reagent dropwise with stirring and adjust the pH to 5.9–8.1 with aqueous 2 *M* ammonia solution. After 30 min, filter the precipitate and wash it with warm (35–40°) water. Weigh the complex containing 2.181% of the metal after drying at 120° for 1 h. Typical results are shown in Table I.

TABLE I

DETERMINATION OF BERYLLIUM BY GRAVIMETRIC AND TITRIMETRIC METHODS

Be taken (mg)	*Gravimetric*			*Titrimetric*	
	Wt. of ppt. (mg)	*Be found (mg)*	*Rel. error (%)*	*Be found (mg)*	*Rel. error (%)*
3.55	162.9	3.55	0.0	3.56	+0.28
	162.2	3.54	−0.28	3.55	0.0
2.90	132.9	2.90	0.0	2.91	+0.34
	132.6	2.89	−0.34	2.92	+0.69
2.84	130.1	2.84	0.0	2.85	+0.35
	130.7	2.85	+0.35	2.84	0.0
2.64	120.4	2.63	−0.38	2.66	+0.75
	121.0	2.64	0.0	2.65	+0.38
1.42	65.5	1.43	+0.70	1.41	−0.70
	65.4	1.43	+0.70	1.42	0.0

When beryllium was determined in the presence of diverse metal ions, 5 ml of 10% (w/v) Na_2EDTA solution were added before the addition of the cyclopentanone-2-carboxyanilide solution.

Procedure for titrimetric determination

Precipitate the beryllium–cyclopentanone-2-carboxyanilide complex as described above, wash, and dissolve it in 20 ml of a (1 + 1) mixture of ethanol and concentrated hydrochloric acid, collecting the solution in a flask fitted with a ground glass stopper. After cooling, add 2–3 g of potassium bromide and dilute with 100 ml of water. Add an excess of the standard 0.1 *N* bromate solution and leave for about 15 min at room temperature. Add 10 ml of a 30% (w/v) potassium iodide solution. After 5 min, rapidly titrate the iodine liberated with standard 0.1 *N* thiosulphate solution. Calculate the metal content on the basis that 1 ml of 0.1 *N* thiosulphate (or bromate) is equivalent to 0.1126 mg of beryllium. The results are given in Table I.

Procedure for spectrophotometric determination.

Dilute an aliquot of the beryllium solution (containing 2.0–6.5 μg) to 5 ml and mix with 2 ml of a Na_2EDTA (100 mg) solution and 1 ml of magnesium sulphate solution containing magnesium equivalent to the EDTA added. Warm the mixture slightly after adding 4 ml of the reagent solution, and adjust the pH to 6.8 or above with aqueous 2*M* ammonia solution. Cool to room temperature, and extract the complex with two 5-ml portions of isobutyl methyl ketone. Measure the absorbance of the combined extracts at 332 nm with the pure solvent as reference.

Procedure for beryl

Fuse about 50 mg of beryl carefully with potassium hydrogen fluoride. Cool the fused mass and treat with sulphuric acid. Heat the mixture to fumes to remove fluoride. Finally, take up with 1.5 *M* sulphuric acid, filter, dilute suitably and precipitate the beryllium–cyclopentanone-2-carboxyanilide complex in the presence of 5 ml of 10% Na_2EDTA solution as described above. Determine beryllium gravimetrically or titrimetrically.

TABLE II

DETERMINATION OF BERYLLIUM IN BERYL

Sample no.	*BeO by standard method* (%)	*Gravimetry*		*Spectrophotometry*	
		BeO (%)	*Rel. error* (%)	*BeO* (%)	*Rel. error* (%)
1	12.37	12.36	−0.08	12.39	+0.16
		12.40	+0.24	12.36	−0.08
2	12.69	12.66	−0.23	12.72	+0.23
		12.68	−0.08	12.75	+0.40

For the spectrophotometric method, decompose 10–20 mg of beryl as above and dilute the resulting solution to 250 ml. Take a suitable aliquot (2 ml) for the spectrophotometric determination in the presence of magnesium–EDTA.

Results obtained for the determination of beryllium in beryl are given in Table II.

RESULTS AND DISCUSSION

Beryllium–cyclopentanone-2-carboxyanilide complex

The colourless complex was dried at 120° and analysed for beryllium by converting it to oxide as well as for nitrogen by the Dumas method. (Found: 2.19% Be, 6.8% N; required for $Be(C_{12}H_{12}NO_2)_2$: 2.18% Be, 6.8% N.) The complex is slightly soluble in ethanol and during its precipitation the alcohol content was kept lower than 10% (v/v). On exposure to light, the complex showed slight blackening owing to decomposition after a few weeks, though it was thermally stable up to 250°.

Effect of reagent concentration

The beryllium complex was precipitated at pH 6.0 with different amounts of the reagent dissolved in ethanol (5% of the final volume). For the process to be quantitative, the supernatant solution after the precipitation should be at least 0.3% with respect to the reagent.

For the extraction method, when the complex was first formed in the aqueous medium, 20 mg of the reagent was sufficient for over 99% extraction in one step. Another extraction with a second batch of 5 ml of isobutyl methyl ketone ensured quantitative transfer. However, much larger quantities of the reagent were required when attempts were made to extract with cyclopentanone-2-carboxyanilide in the organic solvent.

Effect of pH

Beryllium was precipitated from solutions adjusted to different pH values. Precipitation commenced at pH 3.5 and was quantitative between 5.9 and 8.1.

For quantitative extraction of the complex in the presence of magnesium–EDTA the pH range was found to be 7.0–10.5. The percentage extraction decreased very rapidly below pH 7. Care had to be taken to avoid excessive local concentration of ammonia, when this was used to adjust the pH. When the quantity of beryllium was low, especially in case of spectrophotometric determinations, the presence of EDTA was necessary to avoid the effect of local concentration of ammonia.

Absorbance curves and validity of Beer's law

The absorption spectra of the beryllium–cyclopentanone-2-carboxyanilide complex showed a fairly sharp peak at a wavelength of 332–333 nm, at which wavelength the reagent showed no absorbance. Several other solvents, *e.g.* chloroform, tributyl phosphate, amyl alcohols and ether, were tried but isobutyl methyl ketone was chosen because of the ease of extraction and the absence of reagent absorbance at the wavelength of maximal absorbance of the complex. Moreover, the absorbance values remained unchanged even after a week when this solvent was used. Beer's law was found to be valid up to 1.0 μg of beryllium per millilitre of the solvent.

Effect of masking agents

The effects of several common masking agents on the precipitation of beryllium with cyclopentanone-2-carboxyanilide around pH 7.0 were studied. Thioglycolic acid and EDTA did not hinder the precipitation, but sulphosalicylic acid did. Precipitation was incomplete in the presence of phosphoric acid and fluoride and was very slow when tartaric acid was added. In the extraction procedure, only 1 mg of Na_2EDTA could be tolerated, whereas much larger quantities of magnesium–EDTA had no adverse effect.

TABLE III

GRAVIMETRIC DETERMINATION OF BERYLLIUM IN PRESENCE OF DIVERSE IONS

Be taken (mg)	*Diverse ion*[a] *(mg)*		*Be found (mg)*		*Rel. error (%)*	
2.84	Cu^{2+}	50	2.85,	2.84	+0.35,	0.0
2.64	Co^{2+}	50	2.64,	2.63	0.0,	−0.38
2.84	Pb^{2+}	50	2.85,	2.85	+0.35,	+0.35
2.64	Ni^{2+}	50	2.64,	2.64	0.0,	0.0
2.64	Zn^{2+}	50	2.63,	2.64	−0.38,	0.0
2.98	Al^{3+}	30	2.98,	2.98	0.0,	0.0
2.84	Cr^{3+}	50	2.83,	2.83	−0.35,	−0.35
2.98	Fe^{3+}	50	2.97,	2.98	−0.33,	0.0
2.64	Ce^{3+}	30	2.63,	2.64	−0.38,	0.0
2.64	Th^{4+}	50	2.65,	2.64	+0.38,	0.0
2.84	TiO^{2+}	50	2.83,	2.83	−0.35,	−0.35
2.64	VO^{2+}	30	2.64,	2.64	0.0,	0.0
2.98	UO_2^{2+}	30	2.99,	2.98	+0.01,	0.0

[a] In the presence of Na_2EDTA

TABLE IV

SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM IN PRESENCE OF DIVERSE IONS

(Be taken: 6.0 μg)

Diverse ions (mg)			*Be found (μg)*		*Rel. error (%)*	
Ag^{+}	50,	100	6.0,	5.9	0.0,	−1.66
Tl^{+}	60,	100	6.0,	6.1	0.0,	+1.66
Cd^{2+}	60,	100	6.0,	6.0	0.0,	0.0
Cu^{2+}	60,	100	6.1,	5.9	+1.66,	−1.66
Co^{2+}	60,	100	5.9,	5.9	−1.66,	−1.66
Pb^{2+}	60,	100	6.0,	6.0	0.0,	0.0
Hg^{2+}	60,	60	6.0,	6.0	0.0,	0.0
Ni^{2+}	60,	100	6.0,	6.0	0.0,	0.0
Bi^{3+}	60,	60	6.1,	6.1	+1.66,	+1.66
Al^{3+}	50,	100	6.0,	6.0	0.0,	0.0
Ga^{3+}	60,	100	6.0,	6.0	0.0,	0.0
In^{3+}	60,	100	5.9,	6.0	−1.66,	0.0
Cr^{3+}	60,	100	6.0,	6.1	0.0,	+1.66
Fe^{3+}	50,	100	6.0,	6.0	0.0,	0.0
Ce^{3+}	60,	100	6.0,	5.9	0.0,	−1.66
Th^{4+}	60,	100	6.0,	6.1	0.0,	+1.66
Zr^{4+}	60,	60	6.05,	6.0	+0.83,	0.0
TiO^{2+}	60,	80	5.9,	6.1	−1.66,	+1.66
VO^{2+}	60,	100	6.0,	5.9	0.0,	−1.66
MoO_2^{2+}	60,	100	6.1,	6.1	+1.66,	+1.66
UO_2^{2+}	60,	60	6.0,	6.0	0.0,	0.0
WO_4^{2-}	60,	100	5.95,	5.9	−0.83,	−1.66

Effect of diverse ions

Precipitation of beryllium from reasonable quantities of copper(II), cobalt(II), lead(II), nickel(II), aluminium(III), chromium(III), iron(III), cerium(III), thorium (IV), titanium(IV), vanadium(IV) or uranium(VI) was possible when these foreign ions were masked by the addition of 5 ml of 10% Na_2EDTA solution before adding the reagent. The results are presented in Table III.

The results given in Table IV show that the spectrophotometric determination of beryllium after extraction with isobutyl methyl ketone was possible in the presence of appreciable amounts of silver(I), thallium(I), cadmium(II), copper(II), cobalt(II), lead(II), mercury(II), nickel(II), bismuth(III), aluminium(III), gallium(III), indium (III), chromium(III), iron(III), cerium(III), thorium(IV), zirconium(IV), titanium(IV), vanadium(IV), molybdenum(VI), uranium(VI) or tungsten(VI). The amounts of diverse ions indicated in Table IV do not necessarily correspond to the tolerance limit, but were the largest amounts examined.

Optimal concentration range and sensitivity

According to Sandell's definition[14] the optimal concentration range for the spectrophotometric determination of beryllium by the given method was found to be 0.20–0.65 μg of the metal per millilitre of isobutyl methyl ketone, while the sensitivity was $9 \cdot 10^{-4}$ μg cm^{-2}. The molar absorptivity was 9900.

Precision and accuracy

The relative standard deviation for the gravimetric procedure was calculated to be ±0.26%, while the values for the titrimetric and spectrophotometric methods were ±0.66% and ±1.08%, respectively.

The authors are grateful to Prof. S. K. Siddhanta of the University of Burdwan for his kind interest.

SUMMARY

Beryllium in amounts less than 4 mg can be determined gravimetrically with cyclopentanone-2-carboxyanilide in the pH range 5.9–8.1; the relative standard deviation is ±0.26%. Alternatively, the complex can be dissolved in ethanol–hydrochloric acid mixture and determined by titration with bromate. Beryllium in the range 2.0–6.5 μg can be extracted as its complex with cyclopentanone-2-carboxyanilide into isobutyl methyl ketone in the pH range 7.0–10.5; when the absorbance of the extract is measured at 332 nm against pure solvent as reference, the standard deviation is ±1.08 %. When disodium– or magnesium–EDTA is added as masking agent, beryllium can be determined in the presence of Ag(I), Tl(I), Cd(II), Cu(II), Co(II), Pb(II), Hg(II), Ni(II), Zn(II), Bi(III), Al(III), Ga(III), In(III), Cr(III), Fe(III), Ce(III), Th(IV), Zr(IV), Ti(IV), V(IV), Mo(IV), U(VI) or W(VI) either gravimetrically or spectrophotometrically and in most cases by both procedures. Beryllium in beryl can be determined by any of the proposed methods.

RÉSUMÉ

Le béryllium, en quantité inférieure à 4 mg, peut être dosé gravimétriquement au moyen de cyclopentanone-2-carboxyanilide (pH 5.9 à 8.1). Le complexe formé peut être dissous dans un mélange éthanol–acide chlorhydrique, et dosé par titrage à l'aide de bromate. Pour des quantités de 2.0 à 6.5 μg, on peut effectuer une extraction dans l'isobutylméthylcétone, aux pH 7.0 à 10. L'EDTA disodique ou de magnésium peut être utilisé comme agent de masquage; ce qui permet de doser le béryllium en présence de nombreux métaux (Ag, Tl, Cd, Cu, Co, Pb, Hg, Ni, Zn, Bi, Al, Ga, In, Cr, Fe, Ce, Th, Zr, Ti, V, Mo, U, ou W).

ZUSAMMENFASSUNG

Beryllium in Mengen von weniger als 4 mg kann mittels Cyclopentanon-2-carboxyanilid im pH-Bereich 5.9–8.1 gravimetrisch bestimmt werden; die relative Standardabweichung ist ±0.26%. Der Komplex kann auch in einem Äthanol–Salzsäure-Gemisch aufgelöst und durch Titration mit Bromat bestimmt werden. Berylliummengen von 2.0–6.5 μg können als Cyclopentanon-2-carboxyanilid-Komplex im pH-Bereich 7.0–10.5 mit Methylisobutylketon extrahiert werden; wenn die Extinktion des Extraktes bei 332 nm gegen das reine Lösungsmittel als Vergleich gemessen wird, ist die relative Standardabweichung ±1.08%. Bei Zugabe von Dinatrium- oder Magnesium-EDTA als Maskierungsmittel kann Beryllium in Gegenwart von Ag(I), Tl(I), Cd(II), Cu(II), Co(II), Pb(II), Hg(II), Ni(II), Zn(II), Bi(III), Al(III), Ga(III), In(III), Cr(III), Fe(III), Ce(III), Th(IV), Zr(IV), Ti(IV), V(IV), Mo(IV), U(VI) oder W(VI) entweder gravimetrisch oder spektrophotometrisch und in den meisten Fällen nach beiden Methoden bestimmt werden. Für die Bestimmung von Beryllium in Beryll kann jedes der vorgeschlagenen Verfahren angewendet werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THIOSALICYLAMIDE AS A NEW GRAVIMETRIC AND SPECTROPHOTOMETRIC REAGENT FOR PLATINUM

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(Received 18th May 1971)

Sur and Shome[1] have used thiosalicylamide as a reagent for the determination of palladium, rhodium and ruthenium. In the present investigation, it has been employed in the gravimetric and spectrophotometric determination of platinum. Thiosalicylamide reacts with platinum(IV) to give two distinct types of complex; in 1.0–6.0 *M* hydrochloric acid medium, platinum(IV) forms a complex (A) with thiosalicylamide which corresponds to the formula $Pt[(C_7H_6ONS)_2, 2\ C_7H_7ONS]Cl_2$, whereas in acetate medium (pH 4.5–6.0), the reagent reduces platinum(IV) to the bivalent state before the formation of the complex (B), $Pt(C_7H_6ONS)_2$. Both complexes can be weighed directly in order to determine the metal.

Complex A can be extracted with chloroform, in presence of some ethanol, from strongly hydrochloric acid medium. The yellow extract obeys Beer's law at 430 nm. Complex B can be extracted into isobutyl methyl ketone, showing maximum absorbance at 430–440 nm, but its molar absorptivity is much less than that of the complex A, hence only complex A is utilized spectrophotometrically.

EXPERIMENTAL

Apparatus and chemicals

The instrumentation and the preparation of most solutions were the same as described previously.

Chloroplatinic acid (E. Merck) was dissolved in dilute hydrochloric acid, and the solution was standardized by precipitating the metal by the formic acid method. Weaker solutions were made by diluting the stock solution with distilled water.

A 1% solution of thiosalicylamide in 20% ethanol was used for the precipitation of platinum. For spectrophotometric measurements a 0.01 *M* reagent solution in ethanol was used.

Properties of metal complexes

The thiosalicylamide solution when added to a hot solution of platinum(IV) in hydrochloric acid, produced the orange yellow complex A which was found to be soluble in ethanol, chloroform, ether, carbon tetrachloride and in other common organic solvents. It was stable towards nonoxidising acids and was decomposed by alkali. Elemental analysis gave the results: 22.26% Pt, 6.30% N, 14.56% S, 8.10% Cl; required for $[Pt(C_7H_6ONS)_2, 2(C_7H_7ONS)]Cl_2$: 22.21% Pt, 6.38% N, 14.58% S, 8.09% Cl. The complex decomposed at 200°.

A different complex was obtained when platinum(II) was precipitated in hydrochloric acid medium. The complex (C) was yellowish white in colour. Elemental analysis showed the formula to be $Pt(C_7H_7ONS)_4Cl_2$. This complex decomposed at 218°. Platinum in the +4 and +2 states can be precipitated with thiosalicylamide in strongly acidic solutions as complexes A and C, respectively, but the weighing factor for platinum in both cases is practically the same.

The yellowish brown complex B was formed when platinum (IV) reacted with thiosalicylamide in hot acetate solution at pH 5.0–6.0. The precipitate was granular in nature and easily filterable. The complex was fairly soluble in ethanol but was less soluble in chloroform, carbon tetrachloride, benzene and other common organic solvents. The complex was exceedingly soluble in a mixture of ethanol and isobutyl methyl ketone. The complex decomposed at 180–181°. Elemental analysis of the precipitate dried at 140° gave the results: 38.95% Pt, 5.55% N, 6.36% S; required for $Pt(C_7H_6ONS)_2$: 39.08% Pt, 5.61% N and 6.41% S.

GRAVIMETRIC DETERMINATION OF PLATINUM(IV)

Precipitation from highly acidic medium

Platinum(IV) reacted with thiosalicylamide in strongly acidic solution and the metal could be quantitatively precipitated from 1–6 *M* hydrochloric acid solution. Below this range, the precipitate gradually became slimy and difficult to filter. When the acidity was above 6 *M*, the results were low.

The precipitation of platinum was complete when the supernatant liquid contained 0.035% (w/v) of the reagent in excess, the other conditions remaining the same.

TABLE I

DETERMINATION OF PLATINUM IN HIGHLY ACIDIC AND IN ACETATE MEDIA

Precipitation from HCl media				*Precipitation from acetate media*		
Pt taken (mg)	*Wt. of the ppt. (g)*	*Pt found (mg)*	*Error (mg)*	*Wt. of the ppt. (g)*	*Pt found (mg)*	*Error (mg)*
5.70	0.0256	5.69	−0.01			
5.70	0.0257	5.71	+0.01			
11.40	0.0513	11.40	0.00	0.0291	11.37	−0.03
11.40	0.0512	11.37	−0.03	0.0292	11.41	+0.01
14.25	0.0641	14.24	−0.01	0.0365	14.27	+0.02
14.25	0.0640	14.22	−0.03	0.0365	14.27	+0.02
17.10	0.0769	17.08	−0.02	0.0438	17.12	+0.02
17.10	0.0770	17.10	0.00	0.0437	17.08	−0.02
22.80				0.0584	22.82	+0.02
22.80				0.0583	22.79	−0.01

Procedure. Dilute the platinum(IV) solution to 125–150 ml, adjust its acidity 2–3 *M* with respect to hydrochloric acid and warm to 60°. Add 10–15 ml of 1% thiosalicylamide solution and digest the orange yellow precipitate for 30–60 min on a hot water-bath. Filter and wash the precipitate with hot 10% hydrochloric acid on a sintered (no. 4) glass crucible. Dry the precipitate at 110–120° to constant weight, cool in a desiccator and weigh. Typical results are shown in Table I.

Effect of diverse ions. Platinum was precipitated and determined as described above in the presence of many other ions. In the determination of 5.70 mg of platinum, no interference was found from 500 mg of Zn^{2+}, Cd^{2+}, Zr(IV) or Th(IV), 250 mg of Mn^{2+}, Cr^{3+} or Ga^{3+}, 200 mg of Ni^{2+}, Co^{2+}, Al^{3+} or In^{3+}, 100 mg of Ti(IV), U(VI) or Mo(VI), 20 mg of Ir(IV) and 10 mg of Rh^{3+} or Ru^{3+}. Interferences of Os(VIII), Os(VI), Fe^{3+} and V^{5+} were avoided by prior reduction (see below). Palladium, copper and mercury, however, interfered.

Separation of platinum from iron(III), vanadium(V), osmium(VI) and osmium(VIII)

A solution containing platinum(IV) and the diverse ion was diluted to 100 ml. Freshly prepared saturated sulphur dioxide water (20 ml) was added to reduce the metal ions and the acidity was maintained at 2 *M* with respect to hydrochloric acid. The solution was warmed and platinum was precipitated with thiosalicylamide as before. The results are shown in Table II.

TABLE II

SEPARATION OF PLATINUM FROM IRON(III), VANADIUM(V), OSMIUM(VI) AND OSMIUM(VIII) IN HIGHLY ACIDIC MEDIUM

(11.40 mg of platinum(IV) was used in each test. All data are given in mg)

Ion added	Fe^{3+}(500)	V^{5+}(500)	Os^{6+}(7.5)	Os^{6+}(15)	Os^{8+}(10.5)	Os^{8+}(21)
Pt found	11.37	11.40	11.37	11.34	11.40	11.37
Error	−0.03	0.00	−0.03	−0.06	0.00	−0.03

Precipitation from acetate medium

Platinum was completely precipitated with thiosalicylamide between pH 4.0 and 6.5; at lower pH incomplete precipitation occurred. Precipitation was complete when the supernate contained 0.04% (w/v) of thiosalicylamide in excess at pH 5.0. Results obtained by this method are shown in Table I.

Procedure. Dilute the platinum solution to 150 ml and adjust the pH to 5.0–6.5 with sodium acetate. Heat the mixture to 80° and add 10–15 ml of ethanolic 1% thiosalicylamide solution with constant stirring. Digest the yellowish brown precipitate on a hot water-bath for 2 h with occasional stirring. Filter, wash with water and dry at 130–140° to constant weight. Calculate the metal content on the basis that the precipitate (complex B) contains 39.05% of platinum.

Effect of diverse ions. When 17.1 mg of platinum(IV) was precipitated by the above method in the presence of tartrate as masking agent, there was no interference from 200 mg of Ni^{2+}, Co^{2+}, Mn^{2+} or Al^{3+}, 150 mg of Zn^{2+}, W(VI) or Th(IV), 100 mg of Fe^{3+}, Ga^{3+}, In^{3+} or U(VI), 50 mg of Tl^{3+} or V^{5+}, and 20 mg of Ir^{4+}. Interferences of copper and titanium were avoided by masking with EDTA and fluoride ions, respectively, at pH 5.5; up to 50 mg of copper(II) and 60 mg of titanium(IV) could then be tolerated. Rhodium, ruthenium and osmium, however, interfered with the precipitation of the metal.

SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM

The platinum–thiosalicylamide complex (A) formed from varying concentrations of the metal was extracted into chloroform from 3*M* hydrochloric acid solution and the absorbances were measured. The complex showed maximum absorbance at 430 nm (Fig. 1), hence all measurements were carried out at this wavelength.

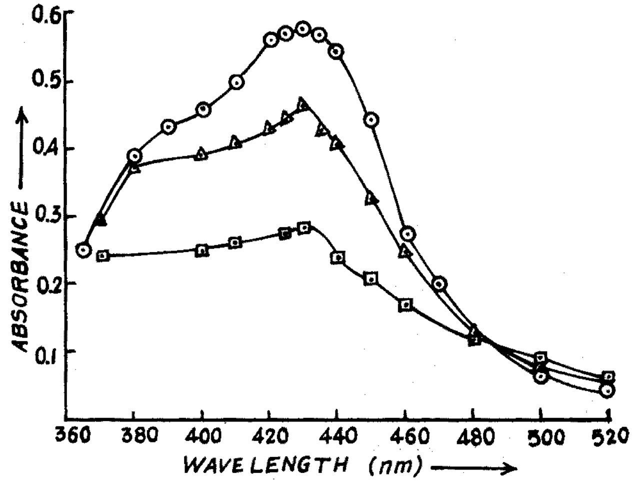

Fig. 1. Absorbance curves of platinum(IV)–thiosalicylamide in chloroform. [Pt]: (⊙) 9.18 μg ml^{-1}; (▲) 7.34 μg ml^{-1}; (▣) 4.59 μg ml^{-1}.

Procedure

Introduce a measured amount of platinum(IV) solution containing 400–500 μg of the metal into a separating funnel and adjust its acidity to 3 *M* in hydrochloric acid. Add 3–5 ml of 0.01 *M* reagent solution and warm the separating funnel with its contents on a boiling water-bath for 5–10 min. Cool the solution, add 10–15 ml of ethanol and extract with 10-ml portions of chloroform. Collect the combined extracts in a 50-ml volumetric flask and make up to the volume with chloroform. Prepare a reagent blank by extracting the aqueous solution at the same acidity with the same quantity of the reagent. Measure the absorbance of the complex at 430 nm, against a reagent blank.

Effect of variables

The colour intensity of the extracted platinum–thiosalicylamide complex in chloroform depended on the acidity of the platinum solution. It was found that the metal was completely extracted from solutions maintained at 4.5 *M* to pH 6.0 with respect to hydrochloric acid, but the colour intensity remained constant only in the range 4.5–3.0 *M*. As the acidity was decreased, the absorption peak gradually moved to lower wavelengths, but above pH 3.0, the peak shifted back to 430 nm. The absorbance again became constant between pH 4.5 and 6.0. These changes in the absorbance were due to the fact that at high acidity the platinum complex A was formed, but with decrease in acidity, the metal was gradually reduced, and above pH 4.5 the platinum complex B was produced. The effect of acidity on absorbance of the platinum–thiosalicylamide complex is shown in Fig. 2.

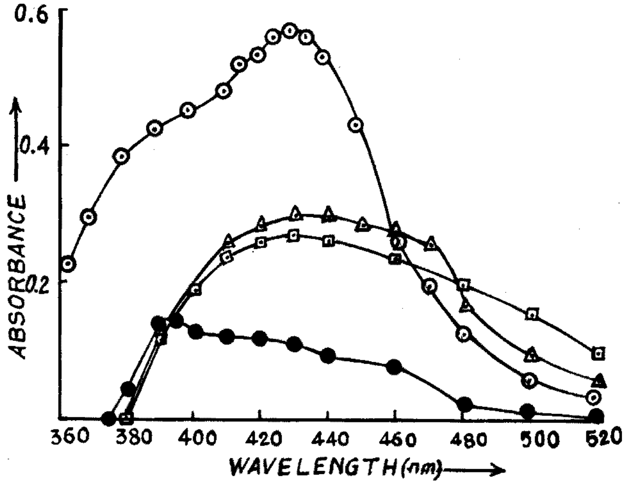

Fig. 2. Absorbance curves of platinum–thiosalicylamide complex in chloroform extracted from different acidities. (⊙) 3.5 M HCl; (●) 0.1 M HCl; (□) pH 1.9; (△) pH 5.14.

The absorbance of the chloroform extract of the platinum–thiosalicylamide complex was found to be quite stable up to 12 h, gradually decreasing thereafter.

Attempts were made to extract the platinum–thiosalicylamide complex with other solvents such as ethyl acetate, isobutyl methyl ketone, carbon tetrachloride and isoamyl alcohol. Extraction with ethyl acetate was very inefficient whereas isobutyl methyl ketone and isoamyl alcohol produced colours with the reagent itself. In carbon tetrachloride the complex was only very slightly soluble.

Conformity of Beer's law and sensitivity

In chloroform the platinum(IV) complex obeyed Beer's law at 430 nm over the concentration range investigated, *i.e.* 2.8–9. 18 μg Pt ml^{-1}.

TABLE III

EFFECT OF FOREIGN IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM

(459.0 μg of platinum was used for each test)

Foreign ion added	*Source*	*Amount tolerated (μg)*	*Foreign ion added*	*Source*	*Amount tolerated (μg)*
Mn^{2+}	$MnSO_4$	2000	UO_2^{2+}	UO_2 acetate	100
Co^{2+}	$CoSO_4$	2000	Mo^{6+}	$(NH_4)_6Mo_7O_{24}$	150
Ni^{2+}	$NiSO_4\cdot 5H_2O$	1000	Th^{4+}	Th acetate	500
Zn^{2+}	$ZnSO_4$	800	Rh^{3+}	$RhCl_3\cdot H_2O$	100
Cd^{2+}	$CdSO_4$	2000	Ru^{3+}	$RuCl_3\cdot H_2O$	100
Al^{3+}	$Al_2(SO_4)_3$	800	Ir^{4+}	$IrCl_4$	100
In^{3+}	$In_2(SO_4)_3$	1000	Pd^{2+}	$PdCl_2$	Nil
Ga^{3+}	$GaCl_3$	500	Au^{3+}	$AuCl_3$	Nil
Cr^{3+}	$Cr_2(SO_4)_3$	500	Cu^{2+}	$CuSO_4$	Nil
Ti^{4+}	$Ti(SO_4)_2$	200			

The molar absorptivity at 430 nm was $1.23 \cdot 10^3$. The sensitivity of the colour system based on Sandell's notation[2] was 0.016 μg cm^{-2}.

Effect of diverse ions

Platinum was determined by the above procedure in the presence of known amounts of various diverse ions. The tolerance limits (Table III) represent the concentrations of the foreign ions in the presence of which the error in absorbance did not exceed ± 2%.

Nature of the complex

The empirical formula of the platinum–thiosalicylamide complex was established by the mole ratio method as described by Meyer and Ayres[3]. The results in Fig. 3 clearly indicate that thiosalicylamide forms a 1:4 complex with platinum(IV).

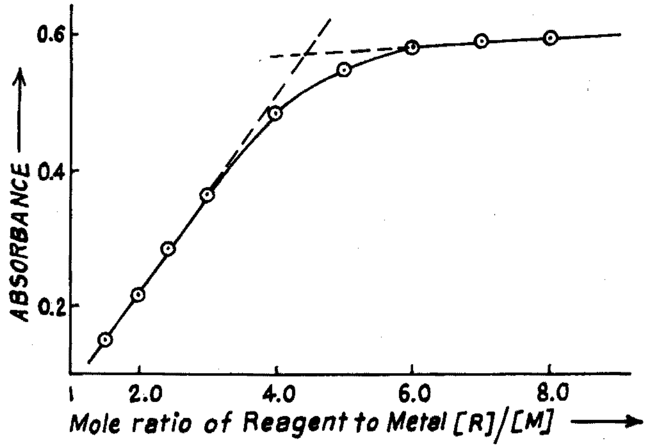

Fig. 3. Composition by mole ratio method applied to platinum(IV)–thiosalicylamide complex.

DISCUSSION

Thiosalicylamide forms two distinct types of complexes with platinum, $Pt[(C_7H_6ONS)_2, 2(C_7H_7ONS)]Cl_2$ (A) and $Pt(C_7H_6ONS)_2$ (B), in highly acidic solution and in acetate medium, respectively. Both complexes are suitable for the direct gravimetric determination of the metal but complex A is preferred because of its large weighing factor. Complex B is, however, more easily filterable owing to its granular nature. Few base metals interfere with the determination in highly acidic medium. In acetate medium, the base metals can be masked by the use of tartrates, fluorides or EDTA. Interference of other noble metals, except palladium, can be avoided either by pH adjustment or by the use of proper reducing agents such as sulphur dioxide. Thiosalicylamide is highly soluble in hot water, hence the excess of reagent can be easily freed from the complex in the gravimetric procedures.

Thiosalicylamide can also be employed for the spectrophotometric determination of platinum(IV). The metal can be determined in both strongly and weakly acidic solutions by the use of the reagent. The advantage of the thiosalicylamide method lies in the fact that platinum can be extracted from 3.0–4.5 *M* hydrochloric acid solution in presence of most of the base metals. The sensitivity and molar absorptivity of the platinum(IV)–thiosalicylamide system are comparable to the corresponding data for the determination of the metal with other organic reagents.

The authors are indebted to the C.S.I.R., New Delhi for a fellowship awarded to K.S.

SUMMARY

Thiosalicylamide has been employed for the gravimetric and spectrophotometric determination of platinum. In highly acidic medium, thiosalicylamide reacts with platinum(IV) to form a complex of molecular formula $Pt[(C_7H_6ONS)_2, 2(C_7H_7ONS)]Cl_2$. In acetate medium $Pt(C_7H_6ONS)_2$ is precipitated. Both complexes are thermally stable and can be weighed directly after drying. Platinum can be determined with thiosalicylamide in presence of Co, Ni, Mn, Zn, Cd, Cr^{3+}, Th, U^{6+}, Mo^{6+}, Rh^{3+} or Ir^{4+} ions from highly acidic medium. Interference of Fe^{3+}, V^{5+}, Os^{6+} or Os^{8+} is avoided by prior reduction. In acetate medium platinum can be precipitated without interference from appreciable amounts of Fe^{3+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Co, Ni, Mn^{2+}, Zn, W^{6+}, Mo^{6+} or U^{6+} with tartrate as masking agent. Copper and titanium are masked by adding EDTA and fluorides, respectively. Osmium(VI) and osmium(VIII) do not interfere after reduction to osmium(IV) with sulphur dioxide.

For spectrophotometric measurements the orange yellow complex formed by platinum(IV) with thiosalicylamide is extracted with chloroform from 3–4.5 *M* hydrochloric acid solution. The chloroform extract shows maximum absorbance at 430 nm; Beer's law is obeyed over the range 2.8–9.18 μg Pt ml^{-1}. The molar absorptivity is $1.23 \cdot 10^3$. There are few interferences.

RÉSUMÉ

On propose la thiosalicylamide pour le dosage gravimétrique et spectrophotométrique du platine. En milieu fortement acide, le platine(IV) donne le complexe $Pt[(C_7H_6ONS)_2, 2(C_7H_7ONS)]Cl_2$. En milieu acétate, on obtient un précipité $Pt(C_7H_6ONS)_2$. Ces deux composés sont stables et peuvent êtres pesés directement après séchage. L'influence de nombreux ions est examinée. En ce qui concerne le dosage spectrophotométrique, le complexe jaune orange obtenu est extrait dans le chloroforme, en milieu acide chlorhydrique 3–4.5 *M*. Maximum d'absorption à 430 nm; la loi de Beer s'applique de 2.8 à 9.18 μg ml^{-1} Pt. Le dosage peut s'effectuer en présence d'un grand nombre d'ions étrangers.

ZUSAMMENFASSUNG

Thiosalicylamid wurde für die gravimetrische und spektrophotometrische Bestimmung von Platin verwendet. In stark saurem Medium reagiert Thiosalicylamid mit Platin(IV) unter Bildung eines Komplexes mit der Formel $Pt[(C_7H_6ONS)_2, 2(C_7H_7ONS)]Cl_2$. In Acetatmedium wird $Pt(C_7H_6ONS)_2$ gefällt. Beide Komplexe sind thermisch stabil und können unmittelbar nach dem Trocknen ausgewogen

werden. Platin kann mit Thiosalicylamid in stark saurem Medium in Gegenwart von Co, Ni, Mn, Zn, Cd, Cr^{3+}, Th, U^{6+}, Mo^{6+}, Rh^{3+} oder Ir^{4+} bestimmt werden. Eine Störung durch Fe^{3+}, V^{5+}, Os^{6+} oder Os^{8+} wird durch vorhergehende Reduktion vermieden. In Acetatmedium kann Platin ohne Störung durch Fe^{3+}, Al, Ga, In, Tl^{3+}, Co, Ni, Mn^{2+}, Zn, W^{6+}, Mo^{6+} oder U^{6+} bei Verwendung von Tartrat als Maskierungsmittel gefällt werden. Kupfer und Titan werden durch Zugabe von EDTA bzw. Fluorid maskiert. Osmium(VI) und Osmium(VIII) stören nicht, wenn sie vorher mit Schwefeldioxid zu Osmium(IV) reduziert werden.

Für spektrophotometrische Messungen wird der von Platin(IV) mit Thiosalicylamid gebildete orangegelbe Komplex aus 3–4.5 *M* salzsaurer Lösung mit Chloroform extrahiert. Der Chloroformextrakt hat bei 430 nm die grösste Extinktion; das Beersche Gesetz ist im Konzentrationsbereich 2.8–9.18 μg Pt ml^{-1} erfüllt. Der molare Extinktionskoeffizient ist 12.3 10^3. Es gibt nur wenige Störungen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

Operating conditions for plasma sources in emission spectroscopy

In the developing field of the use of plasma sources for emission spectroscopy apparently contradictory findings are not infrequent. These include the relative advantages of tangential and laminar gas flows[1] and of the frequency and power employed[2], freedom or otherwise from matrix interference[2,3], detection limits and general operating parameters.

In a recent paper[4] it was reported that the short torch of Greenfield *et al.*[5] gave an increased continuum compared with that produced by a long torch. Since, in a decade of working with plasma sources, our experience has been to the contrary (although we did find, working with a low powered generator, that a long torch gave greater stability[6]), it seemed worthwhile to investigate this particular point further. The results obtained are illustrated in Fig. 1.

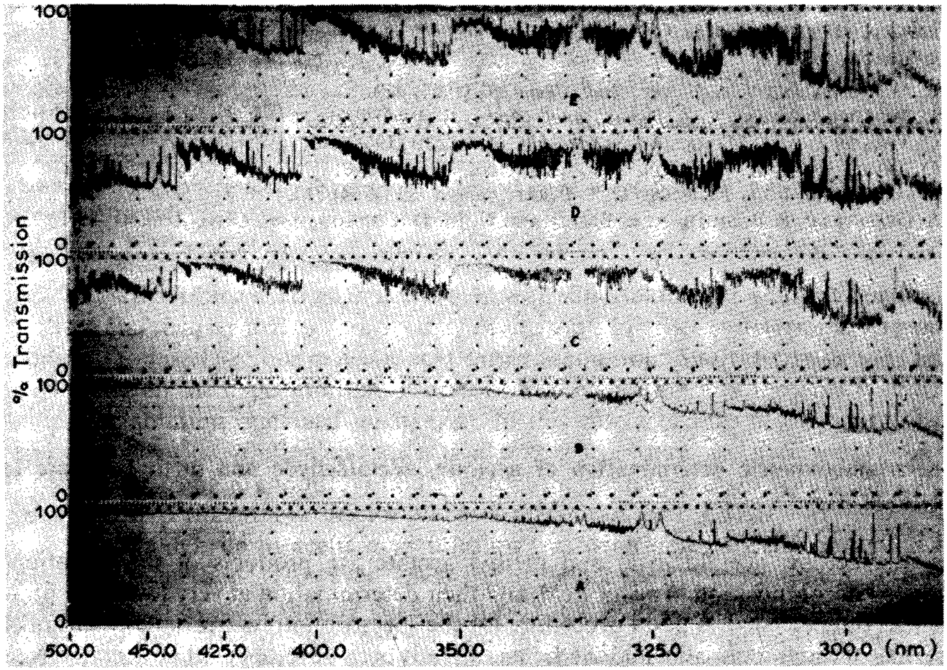

Fig. 1. Spectrum, between 280 nm and 500 nm, of the emission from (A) 30-cm, (B) 4-cm, (C) 2.5-cm and (D) 1.8-cm plasma torches. The length of the torch is measured from the tip of the inner tube to the end of the torch. The torches are 2.5 cm i.d. in all cases. Torch E consists of torch C with an 8-cm long, 5-cm diameter extension tube. Operating conditions: Power generated at work coil 10 kW; power in the plasma 5 kW (by calorimetry); frequency of generator 7 MHz; gas flow: inner tube 15 l min^{-1} argon, outer tube 64 l min^{-1} nitrogen, injector 3.2 l min^{-1} argon. Aerosol: 1% dilute nitric acid solution of bronze. Viewing position: 7.5 cm above inner tube. Ilford N30 plate, exposure 30 sec.

These results show that the background caused by continuum and band structure increases with increasing length of torch, while the signal-to-background intensities for Sn 284.0 nm, Pb 283.3 nm, and others fall. This trend holds over a range of viewing positions of at least 2–5 cm. The emergence of the silicon line at 288.1 nm for the longer torches is indicative of torch burning. Extensive coating of the long torches occurred. The only long torches (*i.e.* those torches where the tail flame emission is viewed through the wall) we have used successfully were those in which the plasma emerged into an extension tube of larger diameter (torch E in Fig. 1).

The modes of operation referred to in this paper[4] such as introduction of aerosols, limits for gas flows and maximal power, are also not completely in accord with our experience nor are they those we would recommend for our equipment.

The lesson to be drawn is that results in this field usually relate only to one particular system running under certain conditions, and that conclusions drawn from one system may not apply if the conditions are varied, nor to other systems. This communication is a plea to potential authors to try to distinguish between features peculiar to their own apparatus and those which might have more universal significance.

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(Received 1st June 1971)

Anal. Chim. Acta, 57 (1971) 209–210

Spectrophotometric determination of acetone, acetaldehyde and methyl acetate in acetic acid

Acetone, acetaldehyde and methyl acetate are products of the radiation-induced decomposition of acetic acid, and their determination at very low concentrations is often needed. A good procedure for the spectrophotometric determination of acetone in water with salicylaldehyde[1] has already been developed, while acetaldehyde may be determined with resorcinol[2] in both water and acetic acid. To determine methyl acetate in acetic acid colorimetrically with potassium permanganate, it was necessary to establish a new procedure based on the reaction of methanol with potassium permanganate[3,4]. The available data refer mainly to the determination of pure compounds. Therefore, in this work, suitable modifications to allow the simultaneous determination of acetone, acetaldehyde and methyl acetate in acetic acid were investigated.

Apparatus and reagents

A Unicam SP 500 spectrophotometer, with 10-mm optical cells was used for absorption measurements. If not specifically stated, the procedures were those recommended in the literature. Where possible, analytical reagent-grade chemicals were used.

Measurements of absorption spectra, determination of percentage absorptivity and validity of Beer's law★

The absorption maximum, percentage absorptivity and validity of Beer's law for each of three reactions used in the present work were determined in acetic acid. For acetone with salicylaldehyde, and for acetaldehyde with resorcinol, aqueous media were also studied to allow comparison with the results found in the literature[1,2]. The results are listed in Table I.

TABLE I

EXPERIMENTAL DATA FOR ACETONE, ACETALDEHYDE AND METHYL ACETATE

Compound	*Solvent*	*Salicylaldehyde*[a]		*Resorcinol*		*Potassium permanganate*	
		λ_{max} (*nm*)	$A^{1\%}_{1cm}\cdot 10^{-3}$	$\lambda = 580$ *nm* $A^{1\%}_{1cm}\cdot 10^{-3}$	*Beer's law range* (*M*)[b]	$\lambda = 640$ *nm* $A^{1\%}_{1cm}\cdot 10^{-3}$	*Beer's law range* (*M*)[b]
Acetone	H_2O	490–495	17.6	—	—	—	—
Acetone	CH_3COOH	490–495	17.6	—	—	13.6	$0.12–1.7\cdot 10^{-5}$
Acetaldehyde	H_2O	—	—	40.1	$0.15–1.5\cdot 10^{-5}$	—	—
Acetaldehyde	CH_3COOH	470	~ 0.8	46.8	$0.15–1.5\cdot 10^{-5}$	3.7	$0.6–1.6\cdot 10^{-5}$
Methyl acetate	CH_3COOH	470	~ 1.37	~ 1.34	—	5.6	$0.6–1.6\cdot 10^{-5}$

[a] Beer's law range for acetone with salicylaldehyde in water and acetic acid is: $0.2–6\cdot 10^{-5}$ *M*. [b] The concentration refers to the solution measured.

Determination of acetone and acetaldehyde

To determine acetone in acetic acid with salicylaldehyde, acetic acid was neutralized and then treated as described by Berntsson[1]. In order to determine very small concentrations of acetone in acetic acid, larger amounts (2–5 ml) of sample were used, depending on the concentration of acetone in the solution, but the final volume of measured solution remained unchanged. In this case a change in the quantities of sodium hydroxide solution and water used in this procedure, was necessary (Table II) to obtain the optimal conditions under which salicylaldehyde dissolves and the colour develops. Experimental errors for all cases did not exceed ±5%.

Acetaldehyde in acetic acid solution was determined by the resorcinol hydrochloride method[2]. However, when the acetaldehyde concentration is very low, it is advisable to use a slightly changed procedure, with 2.75 ml of sample solution, 0.25 ml of $4\cdot 10^{-4}$ *M* fructose solution and 9 ml of reagent solution (1 ml of 0.12 *M* resorcinol solution in 100 ml of concentrated hydrochloric acid)[5]. This provides a more reasonable reference value.

★ For the purpose of comparing results for different components in a mixture, $A^{1\%}_{1cm}$ values (percentage absorptivity) are given: the values were calculated from the formula $A_m = A^{1\%}_{1cm}\cdot c\cdot l$, where A_m is the absorbance measured, l is the cell length and c is the initial concentration in the percentage by weight of substance measured.

TABLE II

AMOUNTS OF SODIUM HYDROXIDE SOLUTION AND WATER USED IN THE DETERMINATION OF ACETONE WITH SALICYLALDEHYDE IN ACETIC ACID

(Into a 25-ml volumetric flask put X ml of test solution, Y_1 ml of NaOH solution, Z ml of water, 0.3 ml of salicylaldehyde and Y_2 ml of NaOH solution. The NaOH solution is 42.5% (w/v) in water)

Sample *X ml*	*NaOH* *Y_1 ml*	*H_2O* *Z ml*	*NaOH* *Y_2 ml*
1	2.5	10	10
2	4	10	To the mark
3	5.5	9	To the mark
4	6	8	To the mark
5	8.5	7	To the mark

Determination of methyl acetate

To establish a procedure for determining methyl acetate the well-known reaction of methanol with potassium permanganate[3,4] in acidic medium was used; methanol is oxidized to formaldehyde, while manganese(VII) is reduced to manganese(II). In the presence of potassium hydroxide methyl acetate is hydrolyzed to methanol and potassium acetate. For solutions of methyl acetate in acetic acid, it is necessary to add potassium hydroxide in excess to neutralize the acetic acid. In the strong alkaline medium, manganese(VII) is reduced to the manganate ion[6,7]; the colour is changed from violet to deep blue, with maximal absorbance at 640 nm. The concentration of methyl acetate can be determined either from the decrease of permanganate concentration measured at 540 nm, or from the amount of manganate formed. Better results were obtained by the latter method.

Acetone and acetaldehyde react with potassium permanganate under the same conditions as methanol, hence it was only possible to determine the total concentration of acetone, acetaldehyde and methyl acetate in the solution. However, since acetone and acetaldehyde can be determined by other methods, the concentration of methyl acetate can be calculated by difference.

Recommended procedure. To a 25-ml volumetric flask add 1 ml of methyl acetate solution, 5 ml of 5 *M* potassium hydroxide solution and, after the mixture has been cooled to room temperature, 1 ml of aqueous 0.5% (w/v) potassium permanganate solution. Leave for 30 min, dilute to volume with water and measure the absorbance at 640 nm against a blank in which acetic acid has been substituted for the methyl acetate solution.

Results

Several mixtures of known composition were analyzed (Table III). The composition of the mixtures is typical of those expected in irradiated samples of acetic acid.

When acetone was determined with salicylaldehyde, a two-fold molar concentration of acetaldehyde had no effect. However, larger amounts caused an absorbance maximum to appear at 470 nm, and the maximum absorbance of acetone was shifted by 15 nm to longer wavelengths. Though this shifted maximum was not very well defined, it was possible to determine acetone with an experimental error of ±5%,

TABLE III

ANALYSIS OF MIXTURES

Composition of mixtures[a]	*Present concn.* · 10^4 (*M*)	% *Error found*[b]
A Acetone	2.9	− 3
Acetaldehyde	1.4	− 1.5
Methyl acetate	2.5	+ 2
B Acetone	1.5	+ 2
Acetaldehyde	0.3	− 7
Methyl acetate	1.7	−10
C Acetone	5.9	− 4
Acetaldehyde	1.4	− 2
Methyl acetate	2.5	+10
D Acetone	1.5	− 5
Acetaldehyde	1.4	− 2
Methyl acetate	1.8	−10

[a] All solutions were in acetic acid. [b] Percentage error is given as a mean value for 5 determinations.

even in the presence of 15-fold amounts of acetaldehyde. Methyl acetate did not interfere even when present in 40-fold amounts.

For the determination of acetaldehyde, acetone and methyl acetate in equivalent amounts have practically no effect. In the presence of a 5-fold amount of acetone, the experimental error for acetaldehyde is −10%, but in the presence of 10-fold amounts of methyl acetate the error does not exceed ±5%.

As can be seen from Table III, fairly good results were obtained when acetone, acetaldehyde and methyl acetate were present in mixtures in equivalent amounts. The error in determining methyl acetate is relatively high because even traces of organic materials present in the solution may interfere with the permanganate method, and because the errors involved in the acetone and acetaldehyde determinations accumulate in the final figure for methyl acetate.

The author wishes to thank Dr. I. G. Draganić and Dr. O. Gal for helpful discussions and criticism of this work.

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(Received 16th May 1971)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

Propriétés chimiques de composés d'uranium dans l'eutectique LiCl–KCl fondu

La spectrophotométrie d'absorption visible et proche i.r. est souvent une méthode de choix pour l'étude des réactions chimiques en sels fondus.

Nous avons examiné plus particulièrement le comportement chimique de l'uranium et de ses composés dans l'eutectique LiCl–KCl fondu et cette étude nous a permis de mettre en évidence de nouvelles réactions et de préciser certains détails pour d'autres déjà décrites dans la littérature.

L'uranium peut se trouver en solution sous les états d'oxydation III, IV, V et VI et dans l'eutectique LiCl–KCl fondu, bien que ces ions s'y trouvent sous forme de complexes chlorés, nous les représenterons, pour faciliter l'écriture, par U(III), U(IV), UO_2(V) et UO_2(VI).

Toutes ces espèces, sauf UO_2(VI), présentent des bandes d'absorption caractéristiques dans le domaine de longueur d'onde considéré (300 à 2,500 nm).

Appareillages

Le dispositif expérimental (fours, boîtes à gants, spectrophotomètre Cary 14 H) ainsi que les différentes manipulations ont été décrits précédemment[1].

Réactifs

Les composés d'uranium utilisés pour préparer les solutions d'U(IV) et d'UO_2(VI) sont respectivement Cs_2UCl_6 et $Cs_2UO_2Cl_4$. Ce choix a été guidé par la stabilité remarquable de ces substances et la facilité avec laquelle on peut les préparer dans un état de grande pureté[2,3].

Les réactions chimiques ont été effectuées au moyen des réactifs gazeux H_2, O_2 et HCl (puretés respectives: 99.99; 99.99 et 99.8%).

Réactions avec l'hydrogène

UO_2(VI). L'ion uranyle(VI) est réduit par l'hydrogène en deux étapes distinctes, la première étant la formation d'uranyle(V):

$$UO_2^{2+} + 1/2\,H_2 + Cl^- \rightarrow UO_2^+ + HCl \qquad (1)$$

UO_2(V) a été mis en évidence dans le bain fondu par les bandes d'absorption caractéristiques déjà signalées par Adams *et al.*[4,5]. Cette réaction ne devient importante qu'au-dessus de 600° et elle nous a permis d'obtenir des solutions relativement concentrées en UO_2(V) ($5 \cdot 10^{-2}$ *M*).

UO_2(V). Le contact prolongé de l'hydrogène avec la solution d'UO_2(V) provoque une réduction subséquente en UO_2:

$$UO_2^+ + 1/2\,H_2 + Cl^- \rightarrow UO_2\downarrow + HCl \qquad (2)$$

UO_2 a été identifié par radiocristallographie.

Il convient de remarquer que l'agitation du bain est requise pour l'observation de la première étape; si on laisse évoluer un bain d'UO_2(VI) sous une atmosphère d'hydrogène, une pellicule d'UO_2 se forme à la surface du bain et on n'observe pas d'UO_2(V).

U(IV). En nous basant sur les données de la littérature[6], nous avons mis en évidence, à température supérieure à 500°, par spectrophotométrie, la réduction de U(IV) en U(III) par l'hydrogène qui s'effectue selon la réaction:

$$U^{4+} + \tfrac{1}{2} H_2 + Cl^- \rightarrow U^{3+} + HCl \qquad (3)$$

Réactions avec l'oxygène

La réaction d'oxydation d'U(IV) par l'oxygène est décrite par Molina[7] de la façon suivante:

$$U^{4+} + O_2 + 2\,Cl^- \rightarrow UO_2^{2+} + Cl_2\uparrow \qquad (4)$$

Nous avons étudié cette réaction à 450° et constaté que UO_2(V) n'apparaît pas comme espèce intermédiaire. Il est possible que l'oxygène oxyde d'abord les chlorures selon la réaction décrite par Mignonsin *et al.*[8]:

$$O_2 + 2\,Cl^- \rightleftharpoons O_2^{2-} + Cl_2 \qquad (5)$$

et que le peroxyde formé oxyde à son tour U(IV):

$$U^{4+} + O_2^{2-} \rightarrow UO_2^{2+} \qquad (6)$$

Cette réaction d'oxydation par l'oxygène est accompagnée de la formation d'ions oxydes[8]

$$O_2 + 4\,Cl^- \rightarrow 2\,O^{2-} + 2\,Cl_2 \qquad (7)$$

qui donnent lieu éventuellement à la précipitation de UO_2, UO_3 ainsi que d'uranates; de plus, ils corrodent fortement les cellules spectrophotométriques.

Réactions avec l'acide chlorhydrique gazeux

UO_2(V). Nos travaux nous ont permis de mettre en évidence l'équilibre de dismutation–amphotérisation réversible de l'uranium pentavalent en présence de HCl à 450°:

$$2\,UO_2^{+} + n\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,W + n\,Cl^- \qquad (8)$$

Dans cette équation, W représente OH^-, H_2O ou H_3O^+ et *n* prend respectivement les valeurs 2, 4 et 6 suivant la pression d'acide chlorhydrique.

En suivant le système par spectrophotométrie, nous observons qu'un bain d'UO_2(V) soumis à l'action de l'acide chlorhydrique voit sa concentration diminuer et que, simultanément, U(IV) apparaît. Une étude chronopotentiométrique complémentaire a montré que UO_2(VI) apparaît en même temps que U(IV).

En réduisant la pression en acide chlorhydrique ou encore en faisant le vide au-dessus du bain, on observe le phénomène inverse: disparition d'U(IV) et d'UO_2(VI) et réapparition d'UO_2(V); cette réaction s'accompagne d'un dégagement d'acide chlorhydrique.

L'eau, sous forme OH^-, H_2O ou H_3O^+ est nécessaire à la réaction d'amphotérisation. A une température supérieure à 500°, cette eau, formée par dismutation, se dégage très lentement et se condense sur les parois froides de la cellule.

Nous avons entrepris l'étude quantitative de la réaction de dismutation–amphotérisation; les résultats seront publiés ultérieurement.

$UO_2(VI)$. A une température supérieure à 600°, $UO_2(VI)$ est réduit en U(IV) en présence d'acide chlorhydrique. Comme l'ont montré Adams *et al.*[4,5], $UO_2(VI)$ oxyde les chlorures du solvant selon la réaction

$$UO_2^{2+} + Cl^- \rightleftharpoons UO_2^{+} + \tfrac{1}{2}\,Cl_2\uparrow \tag{9}$$

et $UO_2(V)$ formé subit ensuite la dismutation selon (8), phénomène mis en évidence par l'apparition des bandes d'absorption d'U(IV).

UO_2. La dissolution de UO_2 par HCl dans l'eutectique LiCl–KCl à 450° a été formulée par Molina[7] de la façon suivante:

$$UO_2\downarrow + 4\,HCl \rightarrow U^{4+} + 2\,H_2O\uparrow + 4\,Cl^- \tag{10}$$

Nous observons, par spectrophotométrie, qu'après dissolution totale de UO_2, environ 50% de l'uranium se retrouvent sous forme d'U(IV) et 50% sous forme d'UO_2(VI). Lorsque les solutions ainsi obtenues sont mises sous vide, U(IV) et $UO_2(VI)$ se transforment en $UO_2(V)$. Ces observations nous ont amenés à proposer la réaction suivante:

$$UO_2\downarrow + HCl \rightarrow UO_2^{+} + \tfrac{1}{2}\,H_2\uparrow + Cl^- \tag{11}$$

suivie de la dismutation d'$UO_2(V)$ sous l'action de HCl selon (8). Faisons observer, pour terminer, que la réaction (11) proposée est l'inverse de la réaction (2) déjà décrite.

Nous remercions l'Institut Interuniversitaire des Sciences Nucléaires et le Fonds National de la Recherche Scientifique pour l'intérêt constant apporté à nos travaux et le soutien financier accordé à notre laboratoire.

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(Reçu le 8 juin 1971)

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

Selective determination of calcium in mineral waters by ring colorimetry

Schiff's bases[1] have been used for many years as chromogenic reagents for the spectrophotometric determination of metal ions. West *et al.* have applied Schiff's bases for highly selective determinations of trace amounts of zinc[2] and vanadium[3] by means of the Weisz Ring Oven method. In the present studies glyoxal bis(*o*-hydroxyanil) has been used for a very selective determination of calcium based on ring colorimetry[4].

Apparatus

A Weisz Ring Oven (National Appliance Co., Portland, Oreg.) was used, with an Agla micrometer syringe for the application of test solution to the paper on the ring oven.

Reagents

Distilled and deionized water, and analytical-grade reagents were used throughout.

Standard calcium solution (1 *mg* ml^{-1}). Dissolve calcium carbonate in the minimum amount of dilute hydrochloric acid, and dilute as required.

Preparation of the reagent. Glyoxal bis(*o*-hydroxyanil) was prepared as described by Goldstein and Stark[5]. For the reagent solution, mix a saturated solution of glyoxal bis(*o*-hydroxyanil) in ethanol, aqueous 10% sodium hydroxide and aqueous 10% sodium carbonate in the ratio 4:1:1. The mixed reagent decomposed on storage, and was prepared freshly each day.

Procedure

Place a circle of Whatman No. 41 filter paper (55 mm diameter) on the ring oven set at 100–110°. Transfer a known volume of the sample solution to the marked centre of the paper circle, and dry the paper. Immerse in 10 ml of 1+1 ammonia solution containing 1 g of ammonium carbonate, to fix the calcium as the carbonate. Shake the paper well and wash thoroughly with water. Remove excess of water by blotting with filter paper and transfer the paper to the ring oven. Wash the calcium ions into the ring zone with 0.1 *M* hydrochloric acid, dry the paper, place it in the reagent bath and withdraw it immediately. Wash the developed paper with water and dry it. A sharp red ring indicates the presence of calcium ions. Compare the in-

TABLE I

DETERMINATION OF CALCIUM

Amount of Ca taken (μg)	*Amount of Ca found* (μg)	% *Error*
0.45	0.46	+2.22
0.25	0.24	−4.00
0.08	0.08	0.00

tensity of the ring visually with a standard scale prepared by taking 1, 3, 5, 7, 9, 11, 13 and 15 μl of a standard calcium(II) solution (0.01 mg ml^{-1}) through the entire procedure.

Typical results are given in Table I.

The range of the proposed determination was found to be 0.02–1 μg of calcium(II) in the total ring; outside this range, visual comparison was difficult.

Determination of calcium in tap water

Evaporate 100 ml of tap water almost to dryness over a low flame. Dilute to 10 ml with demineralized water. Place 1 μl of this solution on the centre of a filter paper set on the ring oven and apply the above procedure. Delhi tap water was found to contain 25 p.p.m. of calcium.

Discussion

Calcium forms a red insoluble chelate[1] with the reagent under the specified conditions. The serious interferences caused by Cu(II), Cd(II), Ni(II) and Co(II) are obviated by fixing calcium(II) as the carbonate at the very beginning; the other metal ions form soluble ammine complexes, and so can be washed out with water.

The interference of various foreign ions was studied by developing rings for calcium(II) with and without the foreign ions taken in varying amounts upto 20 μg.

Ions found not to interfere in the procedure are: NH_4, Li, Na, K, Rb, Cs, Ag, Cu(I, II), Hg(I, II), Cd, Sn(II, IV), Be, Mg, Sr, Ba, Pb(II), Fe(II, III), Ni, Co, Zn, Mn(II), Cr(III), Al, Ga, In, Tl(I, III), Bi, Sb(III, V), As(III, V), Se(IV, VI), Te(IV, VI), Pt(IV), Au(III), V(IV, V), Ge(IV), Ta(V), Mo(VI), UO_2^{2+}, WO_4^{2-}, NO_2^-, NO_3^-, S^{2-}, SO_3^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, Cl^-, Br^-, I^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, CN^-, SCN^-, $C_4H_4O_6^{2-}$ and $C_6H_5O_7^{3-}$.

Cerium and phosphate ions in amounts greater than 3 μg interfered.

The method has proved to be highly selective, sensitive and rapid for the determination of calcium in various samples including mineral water; other ions which are generally present in mineral water either do not interfere or are washed out during the fixing of calcium(II).

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(Received 28th May 1971)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

Determination of tungstate by precipitation of silver tungstate from homogeneous solution

In the determination of tungsten by means of organic reagents, the precipitates usually have no fixed composition and must be ignited to tungsten trioxide. An exception to this rule is the case of oxine and its substitution products. Precipitates of mercury(I) tungstate are liable to contamination with mercury(I) nitrate, but can be ignited to pure tungsten trioxide at 900° ; this precipitation is normally done with mercury(I) nitrate from slightly acidic solution (final pH 3.5)[1], for metatungstate is formed in alkaline media, causing low recoveries, and care is needed to avoid the hydrolysis of the excess precipitant. Precipitation of barium tungstate must be done in absence of air, otherwise about 1% barium carbonate is also precipitated[2] and ignition at 1000° or more then leaves an equivalent amount of barium oxide. Cadmium tungstate precipitates can be dried at 300–400°. Lead tungstate can be precipitated at pH 6.0–6.5, and dried above 110°. In all these methods anions that yield precipitates with the cations used as reagents, *e.g.* sulphate in the determination as lead or barium tungstate, must be absent.

Firsching used diamminosilver(I) as a reagent for the quantitative precipitation of phosphate[3], and for the separation of equimolar mixtures of chloride, bromide and iodide[4]. Varughese and Vaidya[5] found this reagent useful in the precipitation of chromate from homogeneous solution.

In the work described below, the suitability of the reagent for the homogeneous precipitation of tungstate in presence of diverse ions was investigated.

Reagents and equipment

Sodium tungstate (B.D.H. reagent grade) was standardized by the oxine method[6] and used to prepare standard solutions. All other chemicals were of A.R. grade.

A Bausch and Lomb Spectronic 20 colorimeter and a Metrohm E-350 model pH meter were used.

Procedure

Add 0.5 ml of concentrated ammonia solution and 25 ml of 1.0 *M* ammonium nitrate to a sample containing about 0.5 mmole of sodium tungstate and adjust the volume to *ca.* 100 ml. Prepare the precipitant by diluting a mixture of 5 ml of 1.0 *M* silver nitrate solution and 3 ml of concentrated ammonia to about 75 ml. Add this solution to the tungstate solution in one portion. Add concentrated ammonia solution dropwise to remove any turbidity. Now add about 1 ml of ethanolic 0.1 % bromothymol blue indicator.

Heat the beaker on a steam bath for 7–8 h, maintaining the volume by occasional additions of distilled water. The completeness of precipitation is indicated by the fading of the blue colour of the supernate to light green. The pH of the supernate at room temperature was found to be between 6.4 and 7.4. The precipitate began to form after 4 h of heating.

Filter the precipitate on a G_4 sintered glass crucible and wash with small amounts of ice-cold distilled water. Dry at 120° in an oven for about 30 min and weigh.

As a check on the filtrate, the excess of silver(I) was precipitated as silver chloride, which was filtered off. Nitrate was removed from the filtrate by fuming with concentrated sulphuric acid, and the tungsten present was determined in an aliquot by the thiocyanate method[7], the absorbance being measured at 400 nm.

Results and discussion

Ten determinations as silver tungstate gave an average precipitate weight of 255.0 mg compared with an expected value of 254.0 mg; the average error from the expected value was 0.52 % and 300 μg of tungsten remained in the filtrate. In every case the particle size was much larger than that obtained by direct precipitation. Under 450 × magnification, the precipitate obtained by direct mixing was found to be an amorphous powder, whereas the precipitate obtained from homogeneous solution was crystalline and needle-shaped. Filtration and washing were, of course, facilitated by the increased particle size.

TABLE I

EFFECT OF DIVERSE ANIONS ON THE DETERMINATION OF TUNGSTATE AS SILVER TUNGSTATE

No. of detns.	*Substance*		*Weight of silver tungstate (mg)*		*Deviation from true value (%)*
	Taken	*mmoles*	*Mean found*	*True value*	
3	$Na(CH_3COO)$	0.5	255.2	254.0	+0.47
		1.0	249.6		−1.73
3	Na_2SiO_3	0.5	255.2		+0.47
3	$NaNO_3$	50.0	255.0		+0.39
3	KNO_3	50.0	255.4		+0.55
3	Na_2SO_4	15.0	254.9		+0.35
3		20.0	253.2		−0.31
3		25.0	252.0		−0.79
3		30.0	251.6		−0.95
3		35.0	251.0		−1.20
3		40.0	250.2		−1.50
3		50.0	249.4		−1.80

The effect of various anions is shown in Table I. Sodium sulphate did not interfere upto 25.0 mmoles, but with increasing amounts the interference became more pronounced, and with 100.0 mmoles of sodium sulphate the precipitation was only partial. Silicate and acetate interfered if present in excess of 0.5 mmole. Sodium nitrate and potassium nitrate did not interfere even at 50.0 mmoles.

Ammonium sulphate and ammonium acetate hindered the precipitation at all concentrations. The quantity of ammonium nitrate was critical; below 25.0 and above 40.0 mmoles, precipitation was found to be incomplete.

The excess of silver(I) was not critical above a certain limit. When the quantity of silver nitrate was varied from 4.0 to 50.0 mmoles, the determination of 0.55 mmole of tungstate was reproducible within 0.6 %. A value of 5.0 mmoles was selected for routine use.

The final pH of the supernate was not very critical. Satisfactory values were obtained, when the final pH was in the range 6.4–7.4.

No weight loss of silver tungstate was observed after heating for 5 h at 120°, 130°, 140°, 150° or 175°.

The proposed method is quite satisfactory for the determination of tungstate, except in the presence of arsenate, vanadate, chromate, chloride, etc. The gravimetric factor of silver tungstate is very good, and the lack of interference from sulphate is advantageous.

The authors thank the Principal of the Government Engineering College for facilities, and Professor R. P. Shukla for his interest in this work.

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(Received 8th May 1971)

Anal. Chim. Acta, 57 (1971) 219–221

Determination of free cyanide in aqueous solution in presence of complex cyano anions

Since free cyanide can be determined argentimetrically in the presence of kinetically inert hexacyanoferrate(II)[1] or tetracyanonickelate(II) ion[2] which exchange labelled cyanide rapidly[3,4], it seemed desirable to establish which cyano complexes interfere, and which do not, in the determination of free cyanide in aqueous solution by silver nitrate. When a thermodynamically stable and kinetically inert complex cyanide is dissolved in water containing cyanide the equilibrium of the reaction

$$[M^{n+}(CN)_x]^{n-x} + xH_2O \rightleftharpoons [M(H_2O)_x]^{n+} + xCN^-$$

lies far towards the left and the amount of free cyanide in solution remains constant; if the complex cyanide is thermodynamically unstable and labile, the amount of free cyanide in aqueous solution changes. The information about the cyano complexes which do not interfere would have been useful in establishing the stoichiometry of M^{n+}_{aq}–CN^-_{aq} reactions *e.g.*, the Cr:CN ratio has never been properly established in $K_4Cr(CN)_63H_2O$ and the isolation of $K_4V(CN)_72H_2O$[5] creates doubt about the existence of $V(CN)_6^{3-}$ ion[6] in solution. A number of complex cyanides of transition metals which are stable under ordinary conditions and are well characterized have been included in the present study.

Anal. Chim. Acta, 57 (1971) 221–223

Experimental

The cyano complexes $K_4V(CN)_7 2H_2O$[5], $K_3Cr(CN)_6$[7], $K_3Mn(CN)_6$[8], $K_3Co(CN)_6$[9], $K_4Mo(CN)_8 2H_2O$[10], $K_4Ru(CN)_6$[11], $K_3Rh(CN)_6$[12], $K_2Pd(CN)_4H_2O$[13], $K_4W(CN)_8 2H_2O$[14], $K_4Os(CN)_6 3H_2O$[15], $K_3Ir(CN)_6$[16], and $K_2Pt(CN)_4H_2O$[17] were prepared as described in references and were analysed for potassium and cyanide. Potassium was determined as potassium tetraphenylboron[18] and cyanide by the method of Lock and Wilkinson[19]. Analytical results for the complexes are shown in Table I. Analytical-reagent $K_3Fe(CN)_6$ (Merck) was used.

TABLE I

Complex	*% Potassium*		*% Cyanide*	
	Found	*Calcd.*	*Found*	*Calcd.*
$K_4V(CN)_7 2H_2O$	36.52	36.76	41.92	42.79
$K_3Cr(CN)_6$	35.70	36.06	45.42	47.95
$K_3Mn(CN)_6$	35.54	35.74	45.75	47.52
$K_3Co(CN)_6$	35.01	35.31	45.19	46.96
$K_4Mo(CN)_8 2H_2O$	31.32	31.50	40.04	41.9
$K_4Ru(CN)_6$	36.91	37.77	37.41	37.67
$K_3Rh(CN)_6$	31.21	31.18	40.36	41.47
$K_2Pd(CN)_4H_2O$	25.62	25.48	32.14	33.88
$K_4W(CN)_8 2H_2O$	26.42	26.76	34.81	35.62
$K_4Os(CN)_6 3H_2O$	27.94	28.06	26.52	27.99
$K_3Ir(CN)_6$	25.08	25.15	31.47	33.44
$K_2Pt(CN)_4H_2O$	20.04	19.78	26.01	26.30

Standard 0.051 *M*, 0.102 *M* and 0.152 *M* potassium cyanide solutions and 0.05 *M* silver nitrate were used for each complex. The purpose of using potassium cyanide of different concentrations was to observe its effect, if any, on the complex ion. The procedure involved the titration of 25 ml of potassium cyanide with standard silver nitrate as described by Vogel[2]. In further titrations a known weight of the complex was dissolved in 25 ml of the potassium cyanide solution so as to give a 0.1 *M* solution with respect to the complex, and the solution was again titrated with standard silver nitrate. Each titration was carried out at 10-, 15- and 30-min intervals after mixing the cyano complex with the aqueous potassium cyanide. The volume of silver nitrate consumed by 25 ml of potassium cyanide in the presence of $K_4V(CN)_7$-$2H_2O$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_4Mo(CN)_8 2H_2O$, $K_4Ru(CN)_6$, $K_3Rh(CN)_6$, $K_2Pd(CN)_4H_2O$, $K_4W(CN)_8 2H_2O$, $K_4Os(CN)_6 3H_2O$, $K_3Ir(CN)_6$ and $K_2Pt(CN)_4$-H_2O was the same as in the absence of these complexes, showing that they do not interfere. However, variable results were obtained for $K_3Cr(CN)_6$ and $K_3Mn(CN)_6$ which do interfere.

Discussion

Free cyanide can be determined by titration with silver nitrate in the presence of the complex cyano anions which are included in this study, except for hexacyanochromate(III) and hexacyanomanganate(III) ions.

It was expected that potassium hexacyanochromate(III) would not interfere in the determination of free cyanide because $Cr(CN)_6^{3-}$ ion is not attacked by dilute ammonia at ordinary temperatures. But the volume of silver nitrate consumed by aqueous potassium cyanide containing the complex was slightly higher than the amount calculated for free cyanide, although when the titration was carried out very quickly the volume of silver nitrate approached the calculated value. The time dependency and tendency to high results suggests that cyanide is removed from the coordination sphere perhaps owing to aquation which is catalysed by light. The $Mn(CN)_6^{3-}$ ion is stable in aqueous solution containing a slight excess of cyanide. The complex starts hydrolysing during the titration as the free cyanide is removed from the solution, and the presence of ammonia catalyses the hydrolysis, so that the exact end-point cannot be located.

Since the complex cyanides of cobalt(III) and vanadium(III) do not interfere in the determination of free cyanide, it may be possible to extend this work to the determination of cobalt, zinc and cadmium by cyanide methods. Preliminary observation on the interaction of aqueous cyanide with vanadium(II) and vanadium(III) solutions have indicated the existence of hepta-coordinated species of vanadium(II) and vanadium(III) in solution, perhaps $V(CN)_7^{5-}$ and $V(CN)_7^{4-}$ ions.

This work was carried out on the suggestion of Dr. A. G. Sharpe, to whom we wish to express our sincere thanks.

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(Received 5th May 1971)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

Potentiometric study of silver–sulphide reactions in molten alkali thiocyanates

In a previous paper[1] precipitation reactions in molten (Na, K) thiocyanate were investigated, in order to test the feasibility of titration of some cations by monoamperometric technique.

The present communication deals with a potentiometric study of precipitation reactions of silver(I), cadmium(II) and zinc(II) with sulphide electrogenerated by reduction of molten thiocyanate solvent, the determination of the solubility products of the sparingly soluble sulphides, and a study of probable complex formation.

Experimental

Chemicals. Potassium thiocyanate, cadmium acetate dihydrate, zinc acetate dihydrate (Merck), sodium thiocyanate (Fisher), silver sulphate, cadmium and zinc (C. Erba) were of reagent grade and were used without further purification. Mercury was distilled twice *in vacuo.*

Procedure. The measurements were carried out in molten KSCN–NaSCN mixture (73.7 mole % KSCN). Cell, accessories and experimental procedures were the same as previously described[1]. Cadmium and zinc amalgam and silvered platinum were used as indicator electrodes. A soft-glass reference electrode standardized as outlined previously[2] was used.

All the cations were added as pellets of (K, Na) SCN mixture containing a known quantity of metal salts. Amalgam concentrations were about 10^{-4} *M* (mole kg^{-1}); cation concentrations were $3 \cdot 10^{-3}$–10^{-2} *M* .The temperature of the experiments was 155 or 170°. Potentiometric measurements were carried out with a Solartron type LM 1420.2 digital integration voltmeter.

Results and discussion

A typical potentiometric titration curve at $170 \pm 0.2°$ is shown in Fig. 1. The first step can be attributed to the precipitation of metal sulphide, and the second to polysulphide formation between sulphide and sulphur arising from thermal decomposition of the solvent. The polysulphide[3,4] was shown by a cathodic branch in the composite irreversible wave as cited before[1]. This complex has also been observed in chloride eutectic solutions[5].

Systematic studies of the optimal conditions for minimization of polysulphide formation were carried out. For this purpose, the precipitation reaction of silver ion was examined, because silver presents the advantages of a solid reversible electrode. The best results were obtained by decreasing the temperature. At $155 \pm 0.2°$ one step of about 200 mV was observed, corresponding to the Ag_2S precipitation. Subsequently, the titration curve showed another step, of about 80 mV (Fig. 2), and at the same time, the precipitate dissolved and a reddish colour attributable to complex formation appeared.

The end-point corresponding to the precipitation of silver sulphide is considered to be the start of precipitate dissolution. The difference from the equivalence point, calculated from a theoretical plot obtained by neglecting complex formation, was so small that this assumption seems justified. Titration errors were always 5–6% high,

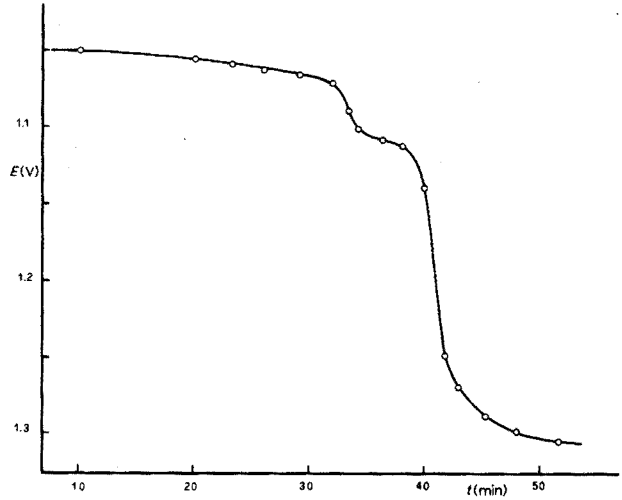

Fig. 1. Potentiometric titration curve at 170 ± 0.2° of $1.584 \cdot 10^{-3}$ *M* silver(I) with electrogenerated sulphide. Current intensity 4.02 mA, $E_{ref} = 0.948$ V.

because of the formation of silver(I) from a slow electrode dissolution as cited elsewhere[2] and in this case emphasized by the presence of sulphide.

All the curves demonstrated that the complex corresponds to the simplest formula $Ag_3S_2^-$. On this assumption, the instability constant (K_i) of this complex in excess of sulphide with respect of the second step (Fig. 2) was calculated; the silver equilibrium concentration was measured from the potentiometric data, assuming $[S^{2-}] = C^0_{S^{2-}} - 2 \cdot [Ag_3S_2^-]$, where $[Ag_3S_2^-]$ is placed equal to $1/3 \cdot C^0_{Ag^+}$ ($C^0_{Ag^+}$, $C^0_{S^{2-}}$ are the total number of g-ions of silver and sulphide added to 1 kg of solvent).

K_{s0} of silver sulphide was calculated by measuring the silver equilibrium concentration from potentiometric data corresponding to precipitate dissolution and

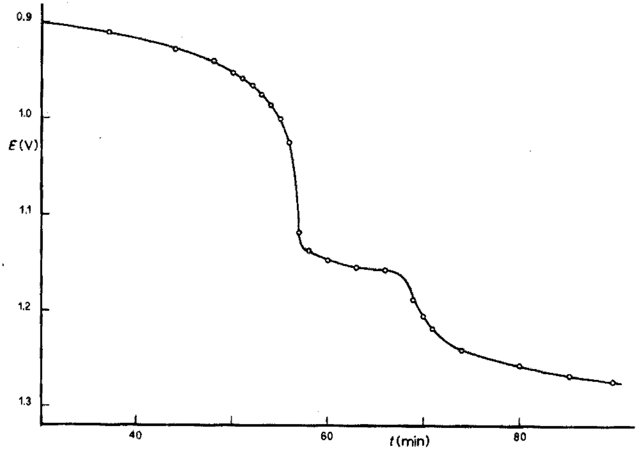

Fig. 2. Potentiometric titration curve at 155 ± 0.2° of $3.312 \cdot 10^{-3}$ *M* silver(I) with electrogenerated sulphide. Current intensity 4.02 mA, $E_{ref} = 0.657$ V.

assuming $[S^{2-}] = \left(\frac{K_i[Ag_3S_2^-]}{[Ag^+]^3}\right)^{\frac{1}{2}}$, where $[Ag_3S_2^-]$ is placed equal to $2 \cdot C^0_{S^{2-}} - C^0_{Ag^+}$. From the same data it is possible to obtain the solubility product (K'_{so}) of the $Ag(Ag_3S_2)$ precipitate; the correlation between the K values is:

$$K'_{so} = K^2_{so}/K_i.$$

Table I shows the $C^0_{Ag^+}/C^0_{S^{2-}}$, K_i, K_{so}, K'_{so} values determined at 155°.

TABLE I

CALCULATED VALUES OF $C^0_{Ag^+}/C^0_{S^{2-}}$, K_i, K_{so} AND K'_{so} AT 155° [a]

$C^0_{Ag^+} \cdot 10^3$ (*mole kg*$^{-1}$)	$C^0_{Ag^+}/C^0_{S^{2-}}$	$K_i \cdot 10^{26}$ (*mole*^{4} *kg*$^{-4}$)	$K_{so} \cdot 10^{18}$ (*mole*^{3} *kg*$^{-3}$)	$K'_{so} \cdot 10^{10}$ (*mole*^{2} *kg*$^{-2}$)
4.958	1.60	1.8	4.5	(11.2)
10.309	1.51	4.0	6.0	9.0
2.995	1.45	(13.0)	8.5	5.6
3.312	1.55	6.2	5.0	4.0
3.079	1.53	3.0	3.4	3.8
Average	1.53	3.7	5.5	5.6

[a] The values in parentheses in the Table are not included in taking the averages.

Similar results were obtained by titrating sulphide with silver ion. In this case, the first step in the curve is due to complex formation and the second to Ag_2S precipitation.

The close connection between the silver–sulphide reaction in molten thiocyanate solvent and the silver–cyanide in water is remarkable.

The data for the potentiometric curve in excess of sulphide ion made it possible to verify the validity of the Nernst equation for the reaction:

$$Ag_3S_2^- + 3e = 3Ag + 2S^{2-}$$

When E was plotted against log $[Ag_3S_2^-]/[S^{2-}]^2$, a straight line with a slope of 28.3 mV (theoretical value 28.6 mV), was obtained. From these considerations it seems impossible to verify the validity of the Nernst equation for the reaction:

$$Ag_2S + 2e = 2Ag + S^{2-}$$

relative to the $Ag/Ag_2S/S^{2-}$ electrode of the second kind. From concentrated solutions of $Ag_3S_2^-$, a reddish compound precipitates. When this is separated from the eutectic solvent by filtration under vacuum, it is unstable to light and in aqueous solution. Further work on this compound is in progress.

This work was supported by the Italian National Research Council. The authors wish to thank Prof. M. Fiorani for his helpful discussion and suggestions.

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Anal. Chim. Acta, 57 (1971) 224–227

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(Received 7th June 1971)

Un solvant acide: $(CH_3COOH)_2BF_3$. Domaine d'électroactivité et niveau d'acidité

L'acidité d'un solvant à hydrogène mobile, tel que l'acide acétique ou l'eau, est considérablement renforcée par l'addition d'un acide de Lewis convenablement choisi en forte concentration[1-6].

Nous nous proposons de comparer les propriétés acido–basiques, oxydo-réductrices ainsi que les propriétés solvatantes de l'acide acétique (AcOH) et du solvant $(AcOH)_2BF_3$ résultant de la combinaison de deux moles d'acide acétique et d'une mole de trifluorure de bore. Ce milieu présente l'avantage d'être stable à la température ordinaire et d'être doué de propriétés physicochimiques très différentes de celles de l'acide acétique[6,7].

L'application des méthodes électrochimiques permet de comparer les domaines de potentiel atteints dans les deux solvants, ainsi que les domaines acides–bases.

Une étude préalable des domaines d'électroactivité à différentes électrodes a conduit aux résultats rassemblés dans le Tableau I. Le domaine de potentiel à l'électrode de platine, d'or, d'argent est très voisin de celui observé dans l'acide trifluoroacétique ou dans l'acide acétique. Dans les meilleures conditions, il est égal à 3.5 V à une électrode de carbone[8].

L'électrode de référence est constituée par le système $Ag(s)/CF_3COOAg$ $5 \cdot 10^{-2}$ *M*. L'allure de la courbe voltampérométrique indique qu'il s'agit d'un système rapide. Nous avons vérifié que la loi de Nernst est suivie lorsque la concentration du trifluoroacétate d'argent varie de $5 \cdot 10^{-3}$ *M* à 10^{-1} *M*.

TABLEAU I

DOMAINE D'ÉLECTROACTIVITÉ DANS $(AcOH)_2BF_3$

(Electrolyte $LiClO_4$ 10^{-1} *M*; électrode de référence Ag/Ag^+ $5 \cdot 10^2$ *M*; vitesse de rotation des électrodes, excepté celle de mercure: 660 tours par min; densité limite de courant: 1 mA cm^{-2})

Electrodes	*Limite (V)*		*Domaine de potentiel (V)*
	Cathodique	*Anodique*	
Platine poli	−0.50	2.05	2.55
Platine platiné	−0.40	1.95	2.35
Or	−0.90	1.95	2.85
Carbone vitreux	−1.30	2.20	3.50
Argent	−1.00	0.00	1.00
Mercure	−1.10	0.00	1.00

Il est nécessaire de faire appel à une hypothèse extrathermodynamique pour établir des corrélations entre les échelles de potentiel et entre les échelles d'acidité obtenues dans des solvants différents. Nous avons retenu celle de Strehlow[9] qui suppose que le potentiel normal du système ferrocène/ferricinium est indépendant de la nature du milieu. Le solvant $(AcOH)_2BF_3$ étant très acide, le ferrocène y est oxydé. On peut néanmoins, à l'électrode à gouttes de mercure, déterminer le potentiel normal de ce système que l'on assimile au potentiel de demi-vague, le système étant rapide. Ce potentiel est égal à -0.691 V par rapport au potentiel de l'électrode de référence. Il est alors possible de comparer les positions relatives du domaine d'électroactivité de l'acide acétique, de l'acide trifluoroacétique et de solvant $(AcOH)_2BF_3$[10,11] (Tableau II). On atteint des milieux beaucoup plus oxydants dans $(AcOH)_2BF_3$ que dans l'acide acétique.

TABLEAU II

COMPARAISON DES DOMAINES D'ÉLECTROACTIVITÉ

(Origine des potentiels: potentiel de demi-vague du système du ferrocène)

Solvants *Electrodes*	$(AcOH)_2BF_3$ $LiClO_4 \cdot 10^{-1}$ *M* *Limites (V)*		*AcOH* $NaClO_4$ 0.5 *M*–*NaAcO* 1 *M* *Limites (V)*		CF_3COOH Et_4NClO_4 0.5 *M* *Limites (V)*	
	Cathodique	*Anodique*	*Cathodique*	*Anodique*	*Cathodique*	*Anodique*
Platine poli	+0.19	+2.74	−0.77	2.02	−0.01	2.79
Platine platiné	+0.29	+2.64	−0.57	1.49	+0.19	2.39
Mercure	−0.41	+0.69	−1.47	0.13	−0.61	0.79

La courbe voltampérométrique relative au système H_2/H^+ dans $(AcOH)_2BF_3$ comme solvant, indique que le milieu est tamponné en acide. Ceci est confirmé par le fait que l'addition d'acide ou de base forts à la concentration 10^{-1} *M* ne provoque pratiquement pas de variation de potentiel. L'équilibre:

$$(AcOH)_2BF_3 \rightleftharpoons AcOH_2^+ + BF_3AcO^-$$

est fortement déplacé vers la droite. Le produit ionique du solvant est égal[8] à $10^{-0.9}$. Des mesures spectrophotométriques confirment ce résultat. Le potentiel pris par l'électrode à hydrogène dans le solvant par rapport au potentiel normal du couple ferrocène/ferricinium permet d'évaluer la fonction d'acidité $R_0(H)$ du solvant pur. Elle est égale à 9.3. Le milieu est donc tamponné et fortement acide. Il serait de 6 unités de pK plus acide qu'une solution molaire d'acide fort dans l'acide acétique[12]. Cela explique que la limite en réduction dans le solvant $(AcOH)_2BF_3$ est décalée de près d'un volt vers les milieux oxydants par rapport à l'acide acétique.

Le milieu étant fortement acide et permettant d'atteindre les milieux fortement oxydants, nous envisageons l'étude de quelques composés fluorés minéraux, susceptibles de se comporter comme des oxydants forts.

Nous tenons à exprimer nos remerciements à Madame Badoz-Lambling, Directeur de Recherche au C.N.R.S., pour l'intérêt qu'elle a bien voulu porter à cette étude, ainsi que le Commissariat à l'Energie Atomique qui a subventionné ces recherches.

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(Reçu le 28 juin 1971)

Anal. Chim. Acta, 57 (1971) 227–229

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

Determination of uranyl nitrate and nitric acid based on in-line density and conductivity measurements

Continuous measurement of the uranium content of process vessels containing uranyl nitrate–nitric acid solutions is an essential part of an automatized uranium control system. Another problem is the control of extraction processes involving these solutions which require that their acidity is always known. These problems may be solved by in-line measurement of level, density and conductivity and subsequent conversion of the three electrical signals to volume, uranium- and acid-concentration values by digital computer processing.

This communication describes experimentally derived equations relating density and conductivity to the two concentrations in the range 200–400 g U l^{-1} and 0.5–1.5 *N* acid. The work is an extension of previous publications on density and conductivity measurements of acid–actinide mixtures[1-3].

Experimental

The in-line conductivity meter used was of the conventional electrode type and was equipped with temperature compensation (Electrofact, cell type 50011, range box type 33240, transmitter type 43200 with 3000 Hz oscillator). The in-line density meter, based on the conventional dip-tube method, was of the industrial type (Foxboro, consotrol D-P cell transmitter, type 613 DM). The current output of their transmitters is between 10 and 50 mA.

The linear relationship between the pressure difference measured by the density meter and the current output was established from values indicated by a precision manometer and measured on the transmitter. The calibration factor relating pressure difference and density was found from measurements on a solution of known density (distilled water) at 20° in the process vessel.

The relationship between the conductance measured by the conductivity meter and the current output was found by replacing the electrodes in the circuit by a variable precision resistance, keeping the thermistor of the cell at 20°. The cell constant relating conductance and conductivity was calculated from measurements on a solution of known conductivity (KCl solution) at 20°[4].

Three levels of uranium concentration (200, 300, 400 g U l^{-1}) and of nitric acid (0.5, 1, 1.5 *N*) were selected. Nine experimental solutions containing different combinations of these concentrations were prepared from standard solutions of uranyl nitrate and nitric acid. The uranium solution was standardized gravimetrically ($s_r = 0.1\%$) and the acid by potentiometric titration with sodium hydroxide ($s_r = 1\%$). The densities at 20° of the nine solutions were precisely determined by weighing a known volume ($s_r = 0.1\%$) and the conductivities at 20° with the in-line instrument ($s_r = 1\%$).

Temperature compensation requires knowledge of the temperature coefficient of the conductivity in the relevant concentration range. These coefficients were determined by measuring the conductivity of four experimental solutions at temperatures around 20°. The thermistor was replaced in the circuit by a resistance equal to its resistance value at 20° during these experiments.

The performance of the in-line measurement system for process solutions was checked by laboratory measurement of the acid and uranium concentrations, by the analytical methods mentioned above.

Results and discussion

The range of the conductivity, K, of the nine solutions was 0.1–0.3 $\text{ohm}^{-1}\,\text{cm}^{-1}$. Regression analysis of the measurements of the conductance ($1/R$ ohm^{-1}) and the current output (i mA) resulted in an equation valid for this particular instrument:

$$\log 1/R = -2.316 + 0.03238\, i - 0.0001762\, i^2$$

The cell constant C ($C = KR$) was found to be 10 cm^{-1}; hence the conductivity could be calculated from:

$$\log K = \log 10 + \log 1/R$$

The measured temperature coefficients (TC) of the conductivity ranged between 1.5 and 2.0 %/°, and could be represented by:

$$TC = 1.8 - 0.5\, H + 0.0004\, U + 0.0014\, HU$$

in which H is the acid concentration in mole l^{-1} and U is the uranium concentration in g l^{-1}. The conductivity measurement was adjusted for a temperature coefficient of 1.8. The temperature correction of the density was neglected, the temperature coefficient being only about 0.05 %/° [5].

Regression analysis[6] of the measured densities D (in g cm^{-3}) and conductivities gave the following relationships:

$$D = 1.0048 + 0.0311\, H + 0.001326\, U$$
$$K = 0.0959 + 0.1983\, H - 0.0000183\, U - 0.000336\, HU$$

The expression shows that the conductivity decreases with increasing uranium concentration in this region and that an interaction term is required to describe the measurements. The two equations may be combined in expressions relating the concentrations and the two measurement values:

$$U = -83.11 + 377.1\, D - SQRT$$
$$H = -28.74 + 16.06\, D + 0.0426\, SQRT$$

in which $SQRT = (142200\, D^2 - 507860\, D + 69882\, K + 447500)^{\frac{1}{2}}$

Three in-line measurements of the uranium concentration of process solutions can be proposed:

(1) Measurement of D only (precision 1%), assuming a constant acid concentration of 1.0 N.

(2) Measurement of D and K (precision of both 1%).

(3) Measurement of D and K, with a more precise in-line density meter* (precision 0.1% and 1%).

Alternative methods for the determination of the acid concentration are:

(4) Measurement of D and K (precision of both 1%).

(5) Measurement of D and K as in method 3 (precision 0.1% and 1%).

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* The Solartron Electronic Group Ltd, Farnborough, England, or Valmet Oy, Instrument Works, Helsinki, Finland.

TABLE I

ERROR ESTIMATES OF THE MEASUREMENT METHODS

Method	*Response*	*Parameter*	*Variation in parameters*	*Variation in response (%)*	*Exper. s_r (%)*
1	*U*	*D*	1%	5.6	2.1
		H fixed	0.2 *N*		
2	*U*	*D*	1%	3.7	1.5
		K	1%		
3	*U*	*D*	0.1%	0.5	0.8
		K	1%		
4	*H*	*D*	1%	4.8	3.6
		K	1%		
5	*H*	*D*	0.1%	2.0	4.1
		K	1%		

Variations in the parameters *D*, *H* and *K*, determining the *U* and *H* concentration, give rise to variations in the responses which can be estimated by a study of the error propagation in the relevant relationships. The results for the middle of the concentration range are summarized in Table I.

The evaluation was verified by measurements on nine process solutions. The precision of the measurements with the described in-line instruments was 1%; a density measurement in the laboratory simulates that of a more precise in-line density meter. The experimental standard deviations of the measurements are listed in the final column of the Table; these deviations agree with prediction.

This work was supported under contract 984/RB with the International Atomic Energy Agency.

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(Received 13th June 1971)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

Determination of chloride in calcium phosphates with a chloride-selective electrode

The use of ion-selective electrodes for the determination of halides is finding increasing application in many fields[1]. Thus, the fluoride-selective electrode used under suitably controlled conditions provides a rapid and accurate means of determining fluoride in both mineralogical and biological samples, as well as in other systems[2]. Whilst the determination of chloride by "conventional" analytical methods causes few of the problems generally associated with the determination of fluoride, the use of a solid-state chloride-selective electrode appears to offer a more rapid and sensitive means for the determination of chloride in solutions where the (a_{Cl^-}) is of the order of 10^{-2}–10^{-5}. From the manufacturer's data[3], it is suggested that the Orion 94–17A chloride electrode may be used directly in aqueous media of pH 0–13, but experience showed that the electrode functioned best under carefully controlled acidic conditions. The technique reported here was developed during a programme involving the elucidation of the solution chemistry of various orthophosphate systems.

Reagents

Dissolution acid. 2 *M* Perchloric acid–2 *M* citric acid. Add 166 ml of A.R. concentrated perchloric acid to a solution of 420 g of A.R. citric acid in 700 ml of deionized distilled water and dilute the mixture to 1 l.

Standard 10^{-1} *M chloride solution.* Dissolve 5.85 g of A.R. sodium chloride and dilute to 1 l with deionized distilled water. Dilute further as required.

Instrumentation

A Radiometer PHM 53 selective ion meter, an Orion 94–17A solid-state chloride electrode, and a Radiometer K601 $HgSO_4$ reference electrode were used. Alternatively, a Hg/KNO_3 ceramic plug reference electrode may be used.

Method

Weigh 0.1–0.2 g of the calcium phosphate into a polythene beaker, and add 5 ml of the dissolution acid. The solid sample is completely dissolved within 5 min. Add 5 ml of 2 *M* triethanolamine (TEA) and 5 ml of water to adjust the pH to *ca.* 2.5. Determine the electrode potential of the system and ascertain the chloride content by reference to a calibration curve constructed from standard sodium chloride solutions, using the same buffer solutions.

Discussion

The use of citric acid in the analysis of calcium phosphates for trace impurities inhibits interference by calcium, which is complexed as the soluble citrate. Many other divalent metals are also complexed, especially the first row transition metals[4]. The use of perchloric acid in the dissolution media was decided from the data for free chloride given in the AnalaR specification[5] ($1 \cdot 10^{-4}$%). Calculation shows that the use of 5 ml of dissolution acid adds but 0.015 p.p.m. of chloride from the perchloric acid.

The conditions used in this determination (*i.e.* pH 2.5) were selected after examination of the results obtained at various pH values. In general, alkaline condi-

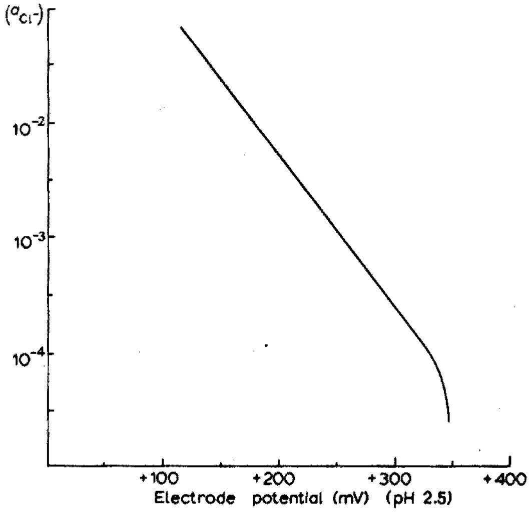

Fig. 1. Typical calibration curve for chloride determination using TEA buffer. K 601 reference electrode.

tions were found to be unfavourable for chloride determination below 10^{-4}. Calibration curves constructed at pH 2.5, 4.7, 6.1 and 6.5 differed only in detail from Fig. 1, except that the detection limit fell with higher pH. The method was used to determine the chloride content in some commercial and laboratory-prepared samples of calcium and divalent transition metal phosphates (Table I). The latter were prepared by mixing solutions of the appropriate metal chloride and disodium hydrogenphosphate at pH 8–10. It was expected that considerable chloride contamination (by incorporation into the orthophosphate structure) would occur.

TABLE I

ANALYSIS OF CALCIUM AND OTHER PHOSPHATES

Sample	*Cl^- (p.p.m.)*	*Average % deviation from the mean*[e]
$CaHPO_4$[a]	24.2	5.27
$CaHPO_4 \cdot 2H_2O$[a]	30.1	3.16
$Ca_5OH(PO_4)_3$[b]	242	1.04
$Ca_5F(PO_4)_3$[c]	520	0.97
Copper(II) fluoride phosphate[d]	2,366	0.76
Copper(II) phosphate chloride[d]	22,047	1.03
$Zn_5OH(PO_4)_3$[d]	330	1.10

[a] ex Knapsack G.m.b.H.
[b] See ref. 6.
[c] See ref. 7.
[d] Laboratory-prepared samples.
[e] Determined by analysis of 8 samples.

The technique described here yields a reproducibility of better than ∓2%, at $(a_{Cl^-}) > 10^{-4}\ M$, if sufficient time is allowed for the attainment of equilibrium between the solution and the electrode system. Normally, for $(a_{Cl^-}) = 10^{-4}\ M$, 5 min is sufficient; at lower activities, 20–30 min may be needed.

Choice of reference electrodes. The use of a ceramic plug calomel reference electrode (Cambridge Instrument Co. Model 42528), a Corning Ag/AgCl reference electrode (Model 476029), a single-junction Orion Model 90–01 reference electrode, both with KCl and KNO_3 filling solution, and a Radiometer K601 $Hg/HgSO_4$ reference electrode were compared. Whilst the ceramic plug calomel reference allowed accurate reproducible results to be obtained in solutions containing more than $5 \cdot 10^{-4}$ *M* chloride, at lower chloride concentrations the results tended to be somewhat erratic because of leakage of filling solution. The Corning Ag/AgCl reference electrode yielded reproducible results over a similar chloride concentration range, but the system required up to 30% more time to reach equilibrium compared with the calomel electrode. The Orion electrode, with an internal filling solution of potassium chloride, was of the sleeve-type construction and leaked its chloride filling solution, which led to high results being obtained. The $Hg/HgSO_4$ electrode was found to be very versatile and to have a short equilibrium response time at $(a_{Cl^-}) > 10^{-4}\ M$. A Hg/KNO_3 ceramic plug reference electrode yielded similar results, but the response time was longer.

Interferences. Calcium(II), dihydrogenphosphate and nitrate did not interfere in 5,000-fold amounts. No interference was found from fluoride in 500-fold amounts or from bromide when the amount of chloride was 300-fold that of bromide. The method has been in use for over six months without apparent effect on the electrode lifetime through possible complexing between TEA and the AgCl detector crystal.

The method described here for the determination of chloride in calcium phosphates should be applicable to the analysis of mineral, chemical and biological samples, as well as solutions.

This work was supported in part by Colgate Palmolive Ltd.

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(Received 7th May 1971).

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK REVIEW

A. K. De, S. M. Khopkar and R. A. Chalmers, *Solvent Extraction of Metal Chelates*, Van Nostrand–Reinhold and Co., Ltd., London, 1970, x+259 pp., price £6.00.

This latest addition to the publisher's series of volumes on various aspects of analytical chemistry covers relevant literature on the technique of solvent extraction, particularly of metal ions.

Attention is given in the earlier parts of the book to chelate-forming reagents, comprising β-diketones, 8-hydroxyquinoline (and derivatives), various oximino compounds, cupferron and its analogues (including N-benzoyl-N-phenylhydroxylamine), nitroso- and pyridylazo-naphthols, dithizone and various dithiocarbamates, xanthates and dithiol. The organo-phosphorus acids, esters and oxides, high-molecular-weight amines and molecular and ion-association compounds are then discussed, and the final part of the book deals with selective extraction procedures for metals.

There is little to commend this book over other more elaborate and authoritative texts. Indeed, the reviewer was under the impression that he had previously seen at least parts of the present text, but it happens that the authors have assumed the same tabular presentation of an earlier well-known text on the same subject. However, the present volume does bring the literature on the application of the more important reagents and procedures up-to-date, and in this respect, the authors might have been commended for a timely compilation, had not the more comprehensive survey of Kertes and Marcus recently been published. However, this is still a useful survey of recent literature in an important field of analytical application; as a supplement to other texts, it should be of value to those interested in the various processes for the solvent extraction of metals.

W. I. Stephen (Birmingham)

Anal. Chim. Acta, 57 (1971) 236

Erratum

A. K. Covington and J. M. Thain, *Anal. Chim. Acta*, 55 (1971) 453–455.

The title of the article reads:
"A simple titration cell–electrode assembly for liquid ion-exchange selective electrodes"

VOL. 57 NO. 1 ANALYTICA CHIMICA ACTA NOVEMBER 1971

CONTENTS

The design and operation of a photon-counting system for analytical atomic spectrometry
D. ALGER, R. M. DAGNALL, B. L. SHARP AND T. S. WEST (London, England) (Rec'd 25th May 1971) 1

Atomic absorption and fluorescence spectroscopy with a carbon filament atom reservoir. Part V. Determination of elements in organic solvents
J. AGGETT AND T. S. WEST (London, England) (Rec'd 15th March 1971) 15

Determination of nanogram quantities of mercury by the reduction–aeration method and atomic fluorescence spectrophotometry
V. I. MUSCAT AND T. J. VICKERS (Tallahassee, Fla., U.S.A.) (Rec'd 7th June 1971) 23

Interferences in the determination of titanium, zirconium, and hafnium by atomic absorption spectrophotometry
V. K. PANDAY (Springvale, Vict., Australia) (Rec'd 12th October 1970). 31

An improved method for the determination of cobalt in biological materials
D. W. DEWEY AND H. R. MARSTON (Adelaide, S.A., Australia) (Rec'd 16th June 1971) 45

Spectrophotometric determination of zirconium in steels with arsenazo III
P. PAKALNS (Lucas Heights, N.S.W., Australia) (Rec'd 15th April 1971) 51

Studies with dithizone. Part XXVII. Primary copper(I) dithizonate
A. M. KIWAN AND H. M. N. H. IRVING (Leeds, England) (Rec'd 23rd June 1971) . 59

Determination of traces of thallium in zinc and zinc-base alloys
P. A. CHAINANI, P. MURUGAIYAN AND CH. VENKATESWARLU (Bombay, India) (Rec'd 1st June 1971) 67

A gas chromatographic method for the determination of low concentrations of the chloride ion
R. BELCHER, J. R. MAJER, J. A. RODRIGUEZ-VAZQUEZ, W. I. STEPHEN AND P. C. UDEN (Birmingham, England) (Rec'd 17th July 1971) 73

Sulphur dioxide as a standard for the determination of sulphur by combustion
B. R. CHAMBERLAIN (Ormskirk, Lancs., England) (Rec'd 15th May 1971) 81

Separation of microgram quantities of dicarboxylic acids by anion-exchange chromatography
L. BENGTSSON AND O. SAMUELSON (Göteborg, Sweden) (Rec'd 15th June 1971) . . 93

Analytical separation of uranium and thorium by liquid anion exchangers
M. COSPITO AND L. RIGALI (Pisa, Italy) (Rec'd 26th May 1971) 107

Determination of thorium in plutonium metal by linear sweep oscillographic polarography
C. E. PLOCK AND J. VASQUEZ (Golden, Colo., U.S.A.) (Rec'd 13th April 1971) . . . 113

Etude potentiométrique et spectrophotométrique de la complexation des ions ferriques par l'acide sulfo-5-salicylique
M. MORIN, M. R. PÂRIS ET J. P. SCHARFF (Lyon, France) (Reçu le 5 juin 1971) . . 123

Transient phenomena of ion-selective membrane electrodes
K. TÓTH, I. GAVALLÉR AND E. PUNGOR (Budapest, Hungary) (Rec'd 15th May 1971) 131

Adsorption of guanine and guanosine at the pyrolytic graphite electrode. Implications for the determination of guanine in the presence of guanosine
G. DRYHURST (Norman, Okla., U.S.A.) (Rec'd 7th June 1971) 137

(continued on page 4 of cover)

Continued from inside page of cover

Coulometric determination of uranium and iron–uranium mixtures with a feedback-controlled electrolysis current
J. E. McCracken, J. C. Guyon (Columbia, Mo., U.S.A.) and W. D. Shults (Oak Ridge, Tenn., U.S.A.) (Rec'd 21st June 1971) 151

Titrimetric determination of uranium with fluorimetric end-point detection
F. H. P. Koning, G. den Boef and H. Poppe (Amsterdam, The Netherlands) (Rec'd 16th May 1971) 159

The precision and accuracy of some current methods for potentiometric end-point determination with reference to a computer-calculated titration curve
T. Anfält and D. Jagner (Göteborg, Sweden) (Rec'd 27th May 1971) 165

A computer-processed semi-automatic titrator for high-precision analysis
T. Anfält and D. Jagner (Göteborg, Sweden) (Rec'd 27th May 1971) 177

A computer-processed high-precision compleximetric titration for the determination of the total alkaline earth metal concentration in sea water
D. Jagner and K. Årén (Göteborg, Sweden) (Rec'd 27th May 1971) 185

Cyclopentanone-2-carboxyanilide as a reagent for the gravimetric, titrimetric and spectrophotometric determination of beryllium
N. K. Chaudhuri and J. Das (Burdwan, W. Bengal, India) (Rec'd 1st May 1971). 193

Thiosalicylamide as a new gravimetric and spectrophotometric reagent for platinum
K. Sur and S. C. Shome (Calcutta, India) (Rec'd 18th May 1971) 201

Short Communications

Operating conditions for plasma sources in emission spectroscopy
S. Greenfield and P. B. Smith (Warley, Worcs., England) (Rec'd 1st June 1971) 209

Spectrophotometric determination of acetone, acetaldehyde and methyl acetate in acetic acid
L. Josimović (Beograd, Yugoslavia) (Rec'd 16th May 1971) 210

Propriétés chimiques de composés d'uranium dans l'eutectique LiCl–KCl fondu
G. Landresse et G. Duyckaerts (Liège, Belgique) (Reçu le 8 juin 1971) 214

Selective determination of calcium in mineral waters by ring colorimetry
K. N. Johri, A. C. Handa and H. C. Mehra (Delhi, India) (Rec'd 28th May 1971) 217

Determination of tungstate by precipitation of silver tungstate from homogeneous solution
K. Varughese and K. S. Rao (Jabalpur, India) (Rec'd 8th May 1971) 219

Determination of free cyanide in aqueous solution in presence of complex cyano anions
A. M. Qureshi and S. A. Khan (Karachi, Pakistan) (Rec'd 5th May 1971) 221

Potentiometric study of silver–sulphide reactions in molten alkali thiocyanates
F. Pucciarelli, P. Cescon and V. Bartocci (Camerino, Italy) (Rec'd 7th June 1971) 224

Un solvant acide: $(CH_3COOH)_2BF_3$. Domaine d'électroactivité et niveau d'acidité
G. Petit et J. Bessière (Paris, France) (Reçu le 28 juin 1971) 227

Determination of uranyl nitrate and nitric acid based on in-line density and conductivity measurements
H. H. Ph. Moeken (Mol, Belgium), J. F. P. Marchand and R. de Vries (Eindhoven, The Netherlands) (Rec'd 13th June 1971) 230

Determination of chloride in calcium phosphates with a chloride-selective electrode
E. J. Duff and J. L. Stuart (Manchester, England) (Rec'd 7th May 1971) 233

Book Review 236

Erratum 236

PRINTED IN THE NETHERLANDS