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Vol. 82, No. 1	March 1976	
Vol. 82, No. 2	April 1976	**(completing Vol. 82)**
Vol. 83	May 1976	**(complete in one issue)**
Vol. 84, No. 1	June 1976	
Vol. 84, No. 2	July 1976	**(completing Vol. 84)**
Vol. 85, No. 1	August 1976	
Vol. 85, No. 2	September 1976	**(completing Vol. 85)**
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PRACTICAL APPROACH TO BACKGROUND CORRECTION AND TEMPERATURE PROGRAMMING IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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(Received 2nd July 1976)

SUMMARY

Step-by-step procedures are outlined for the recognition and removal of errors from incorrect compensation of background absorption in graphite furnace atomic absorption spectrometry. In the case of strong overlap between the specific analyte absorption and non-specific matrix attenuation, careful reconsideration of the temperature program may be required and procedures are outlined for an optimum temperature program to be devised. The application of a rapid observation system is recommended.

Because non-flame atomic absorption spectrometry is essentially a method for trace analysis, the analyte element will frequently be accompanied by an excess of other sample components, which may produce errors in the determination that can broadly be classified in three categories.

(i) *Errors caused by a change in sensitivity [1—3]*. Here the presence of the analyte affects the net absorbance of the analyte or the slope of the analytical curve. This type of error may be corrected by the well-known standard-addition technique and will not be discussed here.

(ii) *Errors caused by non-specific attenuation of hollow-cathode radiation by the matrix [4]*. This type of error, which arises from the overlapping signals of the analyte and the matrix, has lead to the incorporation of deuterium or hydrogen background correctors in virtually all commercial atomic absorption instruments. However, it will be shown that the mere application of the background corrector does not guarantee a correct result and can in fact produce errors in itself. In the first part of this paper, procedures for verifying the correct operation of the background corrector will be outlined.

(iii) *Errors caused by a change in phase transition of the analyte element.* Here the matrix may influence the smooth desolvation of the sample droplet or the volatility of the analyte element [3, 5—8]. This type of error is the most difficult to detect, and can be removed only by a careful reconsideration of the complete temperature program used. In the second part of the paper criteria will be developed and procedures indicated for achieving the correct temperature program for a particular sample.

EXPERIMENTAL

The contents of the present study are based on several years of practical experience with a Perkin-Elmer model 300 atomic absorption spectrometer and a HGA-72 graphite furnace atomizer and temperature programmer. Occasional experience was gained with various other instruments put at our disposal for a limited period by several firms. Therefore, the utility of the proposed procedures is not restricted to one particular instrument.

Graphite tubes with either smooth inner walls or circular grooves were used with the HGA-72.

The absorption signals were displayed on a two-channel Hewlett-Packard recorder model 7402 A with appropriate amplifiers equipped with zero suppression. One channel was coupled to the normal output socket of the spectrometer and displayed the absorbance signal as it would be registered with any ordinary recorder, because the spectrometer amplifier provides the dominant time constant of 0.5 s. The signal for the other channel was taken directly from the rapid preamplifier of the spectrometer behind the photomultiplier tube and thus displayed the transmittance signal without distortion. In fact, the frequency response of the recorder (about 70 Hz) was such that the alternating signal of the hollow-cathode lamp, deuterium lamp and zero transmittance could readily be observed in this channel (compare Figs. 1 and 2). This system thus provided separate observation of the broad-band background attenuation and narrow line absorption, which will be shown to be essential for the present study. Nevertheless, the procedures outlined below will refer as much as possible to the distorted absorbance signal, so that they will be useful for common instruments and recording systems.

RECOGNITION AND REMOVAL OF BACKGROUND CORRECTION ERRORS

The need for background correction in non-flame atomic absorption spectrometry is well known. Depending on the type of atomizer used and on the nature of the analyte and the matrix, there will be a more or less strong overlap of the specific analyte absorption and the non-specific attenuation of radiation caused by the matrix. The term attenuation is preferred for the latter process to incorporate true continuum or molecular absorption as well as scattering of radiation. In general, this overlap is stronger when the residence time of the particles in the atomizer is longer, as is the case in the larger Massmann-type furnaces available from Perkin-Elmer, Beckman, and Instrumentation Laboratories. In the more rapid minifurnaces (Varian-Techtron) this overlap is, in principle, less severe, but this advantage may be obscured by a slow detection and recording system. Consequently, practically all available atomic absorption instruments offer optical background correction facilities. This is usually a deuterium lamp for the ultraviolet and occasionally an iodine lamp for the visible region. The principle of operation was first formulated by Koirtyohann and

Pickett [4] as follows: the signal measured with a hollow-cathode line source is the sum of specific absorption and non-specific attenuation, but the signal from the continuum source reflects only the non-specific attenuation. The difference in these signals therefore equals the specific absorbance, which is then related to the analyte concentration through Beer's law.

However, the practical operation of the background corrector is not as simple as it seems. It is certainly not true that the mere application of the background corrector automatically produces the correct, error-free result of the determination. This is serious as in many cases the output of the instrument (a digitized peak height or complete absorbance peak) appears perfectly normal and contains no indication of a possible error in the background correction. For this reason, we shall summarize the sources of erroneous background correction, the means of detecting such errors and the possibilities of removing them.

Optical misalignment

The first requirement for a true background correction is that the hollow-cathode lamp and the continuum source view the same region of the vaporized sample. If the beams of the two sources do not exactly coincide, then the result will be in error if the sample vapour is distributed inhomogeneously over the atomizer cross-section. This type of error can be readily checked with a wire screen (preferably non-uniform) producing an absorbance of about 0.5. With both sources in operation the net absorbance should remain zero if the screen is moved back and forth or up and down the optical beam. If this is not observed the alignment of the sources should be perfected by the procedure described in the instrument manual.

Excessive background

The background absorbance that can be corrected for is restricted to an upper limit dictated by the spectral bandwidth of the instrument and the electronic circuitry. It should be realized that a subtraction of absorbance is really the ratioing of transmittances and the accuracy of most spectrometers rapidly deteriorates for background absorbances over unity (90 % loss of radiation). Unfortunately, many instruments do not provide an opportunity of measuring the background attenuation signal separately. Consequently, the operator has no direct knowledge of this quantity and the difference signal usually measured can appear deceptively natural.

Figure 1 shows an example of milk analysed for lead. When pure milk is introduced in the graphite furnace, the signal seems perfectly normal and indicates a lead concentration of no less than 0.1 p.p.m. If, however, a twofold diluted milk sample is introduced, the signal does not decrease to 50 % of its original value but disappears completely. This simple check proves that the former signal was a spurious result from incomplete compensation for excessive background attenuation. The separate recordings of the transmittance signals of both sources of radiation (top frames in Fig. 1)

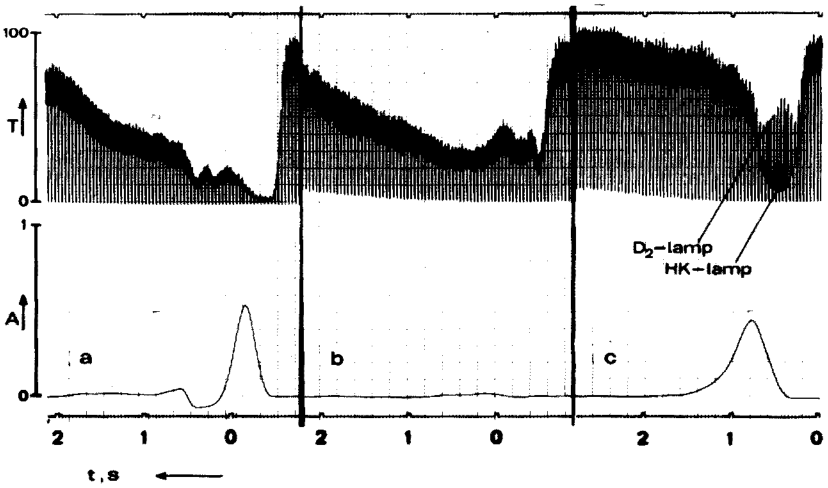

Fig. 1. Determination of lead in milk. (a) 20 μl of pure milk; note spurious absorbance signal; (b) 20 μl of milk/water (1 : 1); (c) 20 μl of milk/water 1 : 2 spiked with 0.1 p.p.m. lead.

demonstrate that, in both cases, the signals from the hollow-cathode lamp and the deuterium lamp are exactly equal. Indeed, if diluted milk is spiked with 0.1 p.p.m. of lead, a true lead signal is faithfully recorded again (Fig. 1c). In order to check whether the background is amenable to correction, Welz [9] recommends the recording of a nearby non-absorbed line (e.g. from the fill gas of the hollow-cathode lamp). If the background is acceptable, the absorbance signal for this line should be zero; if this is not observed, the background is too high. However, such a nearby transition is not always available. Therefore the above procedure, where this type of background correction error is readily detected by recording signals from both the pure sample and the diluted sample and by checking whether or not the signal decreases in proportion to the dilution ratio, is preferred. If the analyte concentration is large enough, this dilution procedure also offers a simple solution to this problem. However, if the sample concentration is close to the detection limit, the inherent loss of sensitivity is not acceptable. An example is offered in the determination of cadmium in rat livers (Fig. 2). The direct introduction of the sample solution produces a background signal that can only be decreased to an acceptable level by a tenfold dilution. The cadmium signal, discernable as a small shoulder to the absorbance signal in Fig. 2a, is then no longer observable. Consequently, dilution offers no solution in this case and the high background must be reduced in another way.

A more general solution to the problem of high background attenuation is the variation of the temperature program to remove the overlap between the background signal and the analyte absorption. This will be discussed below, and it will become clear why this approach is not applicable in the

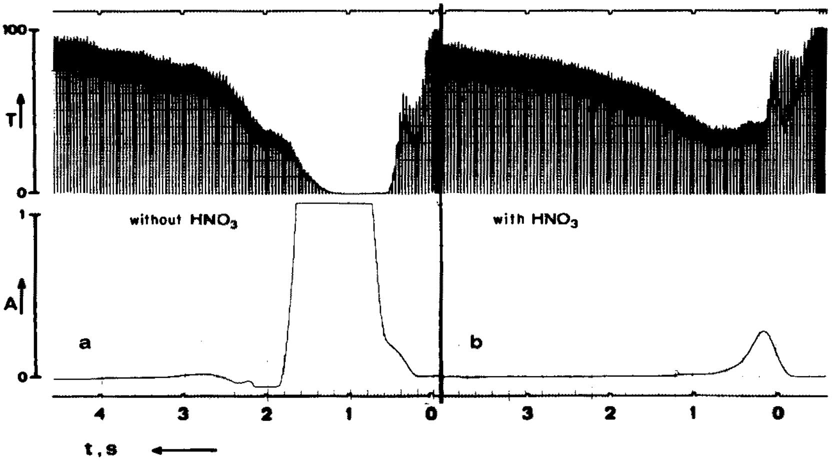

Fig. 2. Determination of cadmium in rat liver extract. (a) Directly and (b) in 2 M nitric acid to reduce strong background attenuation. Transmittance traces in top frames and blank determinations prove the absence of cadmium in nitric acid.

present example. Instead, the background is reduced by the addition of nitric acid. However, the addition of reagents should be considered as a last resort since additional analyte may be present in the added reagent.

Molecular absorption

Up to now the background attenuation has been assumed to be truly continuous, i.e. wavelength-independent. This is generally true for most background signals, since these arise mainly from scattering. In that case the deuterium background correction procedure is feasible in principle. As has been demonstrated by Massmann et al. [10], this is no longer true if the background signal arises from molecular absorption spectra. Because these spectra consist of many narrow rotation lines, the background correction required actually depends on the degree of overlap between the analyte atomic spectral line and one individual molecular rotation line. Because the resolving power of normal atomic absorption spectrometers is much too low to separate the rotation spectra, this degree of overlap cannot be determined and the necessary background correction remains unknown.

In fact, the ordinary deuterium background correction can either overestimate or underestimate the true correction, because the deuterium lamp actually measures an average molecular absorption over the spectral bandwidth of the monochromator. This is illustrated for a hypothetical example in Fig. 3. For analyte line A, which coincides with a strong molecular rotation line, the deuterium signal underestimates the true background absorption at position A. For analyte line B, which falls between two rotation lines, the deuterium signal overestimates the background correction. In both

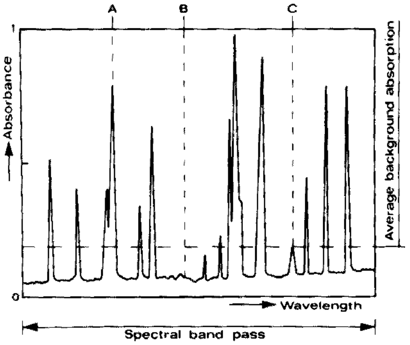

Fig. 3. Schematic representation of molecular absorption spectrum within the spectral band pass of the monochromator. A, B and C are positions of hypothetical analysis lines, for which deuterium background correction (dotted line) is too small, too high and correct, respectively.

cases, the result of the determination is incorrect. For analyte line C, the result would be accidentally correct, because this line coincides with a rotational line that absorbs the hollow-cathode radiation to exactly the same extent as the average absorption measured with the deuterium lamp.

There are two possibilities for checking whether the background attenuation is really continuous and thus amenable to correction with a deuterium source. If the instrument allows the separate recording of the deuterium lamp signal, measurements of the background at slightly different wavelengths will reveal a possible wavelength dependence. If the instrument does not allow such a separate recording, then the sample may be analysed at two or three different slit widths [9]. If the background corrected signal remains independent of the slit width, the background can be safely assumed to be continuous. If it were due to molecular absorption, the background (and hence the background corrected signal) can be expected to vary with the wavelength region selected by the monochromator, because molecular rotation spectra vary with the wavelength (Fig. 3). In performing this test it may be necessary to verify that the matrix-free analyte signal is independent of the slit width. If not, this variation must be taken into account.

Fortunately, molecular absorption is not a very common phenomenon and becomes problematic only in the presence of a large excess of inorganic anions, such as sulphate and phosphate. If the above tests have demonstrated the presence of molecular absorption, the only remedy would be an alteration of the temperature program to separate the analyte signal from the molecular absorption.

In connection with this point, the question arises whether this molecular absorption problem may be overcome by the novel technique of Zeeman-modulation [11, 12], whereby the wavelength of a spectral line is varied through the application of a strong magnetic field. The answer is negative if the magnetic field is applied to the primary source of radiation, i.e. the hollow-cathode lamp [12, 13]. Indeed, this varies the wavelength of the source line, but it does not remove the coincidence of the analyte line and the molecular rotation line in the atomizer cell, which is the source of the error.

In principle, however, the Zeeman modulation technique does offer a solution to this problem if the magnetic field is applied to the absorbing vapour. Because the variation of wavelength with magnetic field is generally different for different spectral lines, it would seem possible to remove the coincidence of the two absorbing lines by applying the magnetic field to the absorbing vapour. However, it is doubtful whether the instrumental effort needed to construct such a system is warranted for the solution of what is essentially a minor and infrequent problem.

CRITERIA AND PROCEDURES FOR THE OPTIMIZATION OF THE TEMPERATURE PROGRAM

The preceding paragraphs have indicated that reconsideration of the temperature program may be required to remove background correction errors. However, this is by no means the only reason for adapting the temperature program to the particular sample at hand. Indeed, it has been noted by several authors [3, 5—8] that the matrix enhances the volatility of an analyte element in such a way that the danger of losses during the ashing step becomes very real. On the other hand, this effect can be put to advantage in the sense that intentional addition of reagents, such as nitric acid or ammonium nitrate, may separate the specific absorption signal from the background attenuation signal [5, 6, 14—19] (Fig. 2). Furthermore, some matrices in our experience strongly influence the desolvation of the sample droplet during the drying step. For those reasons, it should be emphasized that a temperature program cannot be developed for a particular element, but rather for that element in a particular sample and accounting for possible addition of reagents.

Although several reports have been published to demonstrate the influence of the matrix on the volatility of the analyte, there has been no description of a systematic procedure for arriving at the correct temperature program. Therefore, the approach that has been developed over several years of experience with a variety of organic and inorganic matrices will be described. Before discussing the successive steps of the procedure, three criteria used to judge the correctness of each step in the final temperature program are formulated:

(i) *Visual observation of the droplet during the initial stages of the temperature program.* This is extremely useful for checking whether the droplet evaporates smoothly and remains in position during drying. This observation is simple with our equipment where the atomizer can be lifted in front of the instrument by a single movement. In other systems this is not always possible, but the installation of a 45° mirror might offer a solution for many large size graphite tube atomizers.

(ii) *The shape of the transient signal during the atomization step.* Unfortunately, the absorbance signal is practically useless in this respect, because it is too much distorted by the slow electronic processing of most commercial instruments. The undistorted transmittance signal provides much more insight in matrix influence or day-to-day changes, as will be demonstrated below (Fig. 5).

(iii) *The reproducibility of the peak absorbance.* As has been reported by Pinta et al. [6], the reproducibility of the determination is critically affected by the atomization temperature, but it is not restricted to the atomization temperature. The temperatures during the dry and ash steps are also important in this respect. Finally, the long-term validity of the temperature program can also be checked by running standard samples periodically and checking their reproducibility.

Initial temperature program

The starting point for the temperature program is obtained from a solution of the element in water. The drying step is independent of the element under consideration and normally amounts to 30 s at about 85 °C for a 20-μl sample. The ashing step takes 20 s at the highest temperature permitted without loss of the analyte and, analogously, the atomization temperature is a narrow safety margin above the lowest temperature for which the analyte reaches its maximum absorbance [20]. Because the ultimate temperature program must nearly always be adjusted for each sample, there is no point in a detailed optimization of this initial program. For the same reason no temporal variation of the temperature between the three consecutive steps is employed.

A novel sample is then first subjected to the initial three-step program available for the analyte. The sample droplet is observed visually during the drying step, and the transmittance signal recorded during the atomization step is inspected for peak shape, peak position and the height of the background relative to the specific peak absorption. In rare cases the initial program is usable as such, but normally changes are required as will be described below.

Drying temperature

In the pure aqueous solution the droplet is seen to evaporate smoothly and disappear completely during drying at about 85 °C. With the sample solution visual observation may reveal three problems:

(i) sputtering of the droplet and random ejection of particles over the volume of the graphite furnace;

(ii) incomplete drying so that the droplet has not disappeared at the end of the drying step;

(iii) spreading of the droplet over the inner surface of the graphite tube.

All three effects lead to a poor reproducibility of the final result and must, therefore, be prevented. This is done in two ways. First, the drying temperature is reduced to prevent sputtering or spreading of the droplet as can be observed by visual inspection: the droplet remains in position and diminishes gradually. However, this reduction of the drying temperature retards the desolvation so that generally the drying period must be lengthened to evaporate the droplet completely. Sometimes this is insufficient and even after prolonged drying a viscous precipitate is seen to remain. In that case the temperature is no longer raised stepwise to the ashing temperature, as was done in the pure water solution, but is allowed to increase gradually towards the ashing temperature (ramp programming). This gradual increase must be slow enough to prevent sputtering and spreading of the droplet, which is again judged from visual observation (until the tube radiation makes this impossible), or from cracking sounds and ultimately from the absorbance signal itself. For this last check it may be necessary to add some analyte to the sample to make sure that an absorbance signal is observed.

Ashing temperature

It is the purpose of the ashing step to remove as much of the matrix as possible without loss of the analyte. Visual observation is no longer possible and recourse must be made to the absorbance signal observed during the atomization step, which has been maintained at its initial value so far. If the background signal is small enough, the final ashing temperature is readily derived by the same procedure as outlined for the pure aqueous solution. A temperature is then selected which is slightly below the highest temperature permitted without loss of the analyte, visible from a reduction of the absorbance signal. The necessity of checking the initial ashing temperature for matrix influences has been amply demonstrated in the literature [3, 5–8]. Indeed, it has also been our experience that matrices such as milk and chloride, may require a significant reduction of initial ashing temperature to prevent analyte losses. Simultaneously, however, this enhances the possibility of excessive background signals because of incomplete volatilization of the matrix.

Here again the limited utility of the absorbance signal becomes evident, because it obscures the temporal separation of the specific analyte absorption peak from the background attenuation signal during the atomization step. Indeed, the relative position of the two signals is essential for predicting the extent to which temperature programming can reduce an excessive background.

As an example, Fig. 4 shows the determination of lead in liver extract. With the initially low ashing temperature, an excessive background signal is observed, and this must be reduced. However, the transmittance signal of the hollow-cathode lamp reveals that the specific lead absorption occurs before the matrix absorption signal. Therefore, a further increase in ashing temperature is unacceptable, because the more volatile analyte will then be lost together with the matrix. As was the case for the example shown in Fig. 2a, an attempt must be made to alter the relative volatility of the

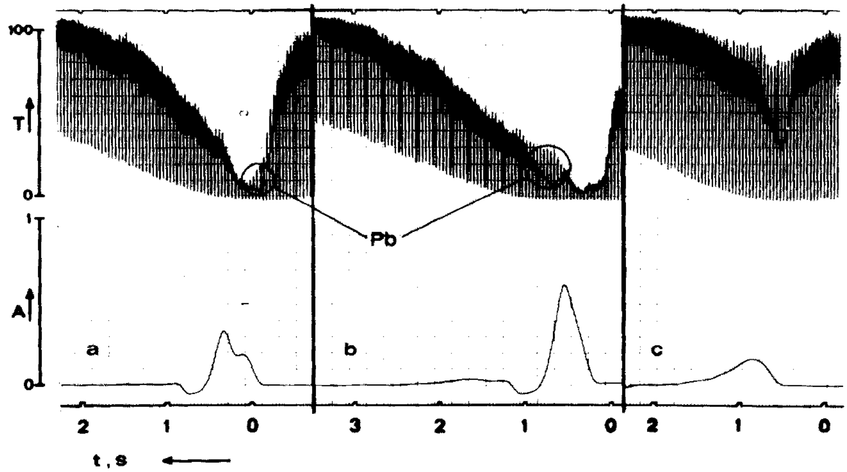

Fig. 4. Determination of lead in rat liver extract. (a) 10 μl of pure extract; nominal ashing temperature 700 K; background too high. (b) Same ashing temperature; 20 μl of extract with ammonia liquor (1 : 4); ammonia is added to retard the volatilization of lead. (c) 20 μl of extract with ammonia liquor (1 : 4); nominal ashing temperature raised to 800 K to reduce the background.

analyte and the matrix by the addition of certain reagents. Several examples of this procedure have been described in the literature. Frech [8] added ammonia to retard the volatilization of bismuth. Ediger [16] reduced the volatility of selenium, cadmium and mercury by the addition of various salts. A similar effect of molybdenum on selenium was reported by Henn [14] and the favourable influence of acids has been noted by several authors [7, 8, 18, 19]. Obviously, the chemicals added must be checked for contamination with the element.

In the present example the addition of ammonia is seen to interchange the volatility of the matrix and the analyte lead (Fig. 4b). If this could have been observed directly, the addition of chemicals would not have been necessary. The background is still too high, but now the ashing temperature can be safely raised to reduce it without running the danger of losing the analyte (Fig. 4c).

The addition of ammonia in this case also raises the sensitivity of the determination. Despite a fivefold dilution, the signal returns to its original value with only a twofold increase in sample volume (compare the absorbance signals in Figs. 4a and 4c). Indeed, standard addition is no longer necessary, and all analyses can be run against aqueous references. The example shown in Fig. 4 demonstrates the importance of a separate recording of the background signal. Furthermore, the continuous observation of the undistorted transmittance signals offers a substantial reduction in effort and time spent in optimizing the ashing temperature. Indeed, the mere observation of a "background-corrected" absorbance signal (bottom frames in Fig. 4), does not permit suitable conditions for this analysis to be reached.

Atomization temperature

After the reduction of the background signal to an acceptable level by the selection of a proper ashing temperature, the determination of the final atomization temperature is relatively simple. Minor variations of the initial atomization temperature show, through a change of peak absorbance or peak shape, whether the atomization of the analyte is complete. Precise adjustment of the atomization temperature is judged from the reproducibility obtained in successive recordings of a single sample solution.

It should be noted that ramp programming is not employed between ashing and atomizing of the sample. In our experience this is seldom, if ever, of advantage, because the ashing temperature is usually very close to the maximum value before analyte losses occur. A gradual increase of the temperature after the ashing step would then immediately give rise to a slow release of the analyte atoms, so that the absorption signal would become very broad and would, therefore, be reduced in sensitivity. Moreover, the low drying and ashing temperatures are reached very rapidly, but the generally high atomization temperature is approached much more slowly by the graphite tube. Indeed, the investigation of Maessen and Posma [21] demonstrates that the signal is usually observed while the graphite tube is still being heated up to its final temperature. In other words, the heat capacity of the atomizer is so large that it provides for ramp programming during the atomization step by itself.

Final temperature program in operation

After all the time spent in developing his final temperature program, the analyst may hope to relax and process his samples. Unfortunately, this is not true and he should remain vigilant in continuously checking his results. Figure 5 is an example where the results unexpectedly deteriorated for exactly the same sample and temperature program. Because the shape of the absorbance signal (but not the transmittance signal!) remains deceptively unaltered, such accidental changes can only be detected by poor reproducibility of the peak absorbance.

Two causes may be advanced as being responsible for this and similar observations. The inner wall of the graphite tube may be attacked by the sample and traces of the sample may remain and accumulate in the tube even after the tube has been annealed after each run. This latter factor is responsible for the deviations shown in Fig. 5. Cleaning of the inner wall of the tube with a piece of cotton and methanol (being careful not to damage the grooved tubes) may bring temporary relief. Gradual variations of the temperature program may also prolong the useful life-time of a graphite tube. Obviously, however, graphite tubes have a finite life-time and must be exchanged from time to time. Unfortunately, with each new tube the temperature program must be checked again, at least with difficult samples.

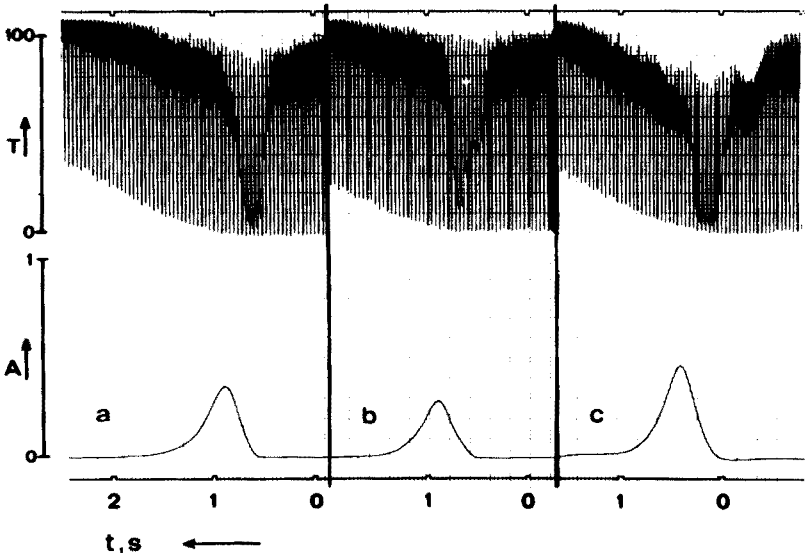

Fig. 5. Triplicate determination of lead in a single rat liver sample under constant, optimized conditions (Fig. 4c) to illustrate a sudden deterioration of the precision.

CONCLUSION

This report has shown that analyses with the graphite furnace atomic absorption technique are not straightforward in the case of trace analysis with a large amount of matrix. The validity of the background correction which is applied and is generally necessary, must be checked, and great care must be taken to arrive at the temperature program adapted to the analyte under consideration in a particular sample. However, with these considerations, very good results can be obtained. Indeed, it is possible on a routine basis to reach reproducibilities better than 0.01 absorbance units, which is fully comparable to flame atomic absorption spectrometry.

REFERENCES

1 G. Baudin, M. Chaput and L. Feve, Spectrochim. Acta, 26 (1971) 425.
2 R. B. Cruz and J. C. van Loon, Anal. Chim. Acta, 72 (1974) 231.
3 J. Smeyers-Verbeke, Y. Michotte, P. van den Winkel and D. L. Massart, Anal. Chem., 48 (1976) 125.
4 S. R. Koirtyohann and E. E. Picket, Anal. Chem., 37 (1965) 601.
5 M. Pinta and C. Riandey, Analusis, 3 (1975) 86.
6 C. Riandey, P. Linhares and M. Pinta, Analusis, 3 (1975) 303.
7 W. Frech, Anal. Chim. Acta, 77 (1975) 43.
8 W. Frech, Z. Anal. Chem., 275 (1975) 353.
9 B. Welz, Atom Absorptions-Spektroskopie, Auflage 2, Verlag Chemie, Weinheim, 1975.
10 H. Massmann, Z. Ed. Gohary, Proc XVIII CSI, 1975, p. 557.
11 H. Koizumi and K. Yasuda, Anal. Chem., 47 (1975) 1679.

12 H. Koizumi and K. Yasuda, Spectrochim. Acta, 31B (1976) 237.
13 R. Stephens and D. E. Ryan, Talanta, 22 (1975) 655.
14 E. L. Henn, Anal. Chem., 47 (1975) 428.
15 T. D. Martin, J. F. Kopp and R. D. Ediger, At. Absorpt. Newslett., 14 (1975) 109.
16 R. D. Ediger, At. Absorpt. Newslett., 14 (1975) 127.
17 L. A. Briese and J. P. Giesy, At. Absorpt. Newslett., 14 (1975) 127.
18 V. P. Garnys and L. E. Smythe, Talanta, 22 (1975) 881.
19 C. W. Fuller, Anal. Chim. Acta, 81 (1976) 199.
20 B. Welz, Proc. XVII Colloq. Inter. Spectrosc., Florence, (1973) 67.
21 F. J. M. J. Maessen and F. D. Posma, Anal. Chem., 46 (1975) 1439.

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STANDARDIZATION OF METHODS FOR THE DETERMINATION OF TRACES OF MERCURY
PART III. DETERMINATION OF TOTAL MERCURY IN CHLORINE

A REPORT PREPARED BY THE MERCURY ANALYSIS WORKING PARTY OF THE BUREAU INTERNATIONAL TECHNIQUE DU CHLORE*

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SUMMARY

A method is given for the routine determination of mercury in chlorine. For liquid chlorine, a sample is taken in a refrigerated trap containing hydrochloric acid. The chlorine is slowly evaporated at atmospheric pressure, and the hydrochloric acid remaining is washed with carbon tetrachloride to remove organic substances. The mercury remains in the aqueous phase and is finally determined by flameless atomic absorption spectrometry. Gaseous chlorine is sampled in an evacuated bulb and the mercury absorbed in an acid permanganate solution, before its determination by flameless atomic absorption spectrometry.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben zur Routinebestimmung von Quecksilber in Chlor. Flüssiges Chlor wird in ein gekühltes Gefäss gebracht, dass Salzsäure enthält. Das Chlor wird verdampft bei atmosphärischem Druck. Die zurückgebliebene Salzsäure wird mit Tetrachlorkohlenstoff extrahiert um organische Verunreinigungen zu entfernen. Das Quecksilber bleibt in der wässrigen Phase und wird bestimmt mit flammenlosen Atomabsorption. Gasförmige Chlorproben werden genommen in eine Gasmaus und das Quecksilber wird absorbiert in saures Permanganat. Das Quecksilber wird bestimmt mit flammenlosen Atomabsorption.

RÉSUMÉ

On décrit une méthode permettant la détermination du mercure en analyse de routine de chlore. Le chlore liquide est introduit dans un piège refroidi contenant de l'acide chlorhydrique. Il est alors évaporé à la pression atmosphérique. Les substances organiques que renferme le résidu d'évaporation sont extraités par lavage au tétrachlorure de carbone.

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*The members of the Working Party responsible for the preparation of this report were R. Ankersmit, J. Barjhoux, R. Bult, F. Cappellina, W. T. Carter, W. Dürr, Ch. Killens, P. Mélard, S. A. Norberg, F. Nouyrigat, M. Olivier, P. Reiners and H. Romeis. This report has been approved by the General Technical Committee of the BITC, which also authorized its publication.

Le mercure restera dans la phase aqueuse et est déterminé par absorption atomique sans flamme. Pour le chlore gaseux, la prise d'échantillon est effectuée en ampoule et le mercure est absorbé dans permanganate acide. Le mercure est déterminé par absorption atomique sans flamme.

In this series [1, 2] on the standardization of analytical methods for the determination of traces of mercury, the present paper describes the determination of mercury in chlorine. As in the earlier methods [1, 2], the mercury content is measured by flameless atomic absorption spectrometry. The main part of this paper is concerned with the sampling and preparation of chlorine samples for the mercury determination.

CHOICE OF SAMPLE PRETREATMENT

When mercury is present in chlorine, it will be in inorganic forms, and mainly as mercury(II) chloride, $HgCl_2$. Indeed, chlorine is sometimes used as a reagent to convert organic mercury compounds to inorganic compounds for the determination of mercury. Calomel, Hg_2Cl_2, dissociates in the gaseous phase to mercury(II) chloride and mercury. With an excess of chlorine, the free mercury is attacked so that all mercury is finally converted to sublimate ($HgCl_2$). The vapour pressures of the inorganic mercury compounds are low. At 25 °C, calculated from data given by Washburn [3], the maximum concentrations in chlorine gas, given for a chlorine pressure of 1 atm., are:

free, atomic mercury	20	mg Hg m^{-3};	7	mg Hg kg^{-1} Cl_2
sublimate, $HgCl_2$	1	mg Hg m^{-3};	0.4	mg Hg kg^{-1} Cl_2
calomel, Hg_2Cl_2	0.04	mg Hg m^{-3};	0.016	mg Hg kg^{-1} Cl_2

For the determination of total mercury in chlorine by flameless atomic absorption spectrometry, it is necessary to remove the large excess of chlorine. For liquid chlorine, this can be done by evaporating the chlorine. Because of the low mercury concentration, the low volatility of mercury(II) chloride and the low temperature, this will not cause losses of mercury. Only in the last stage, when the last chlorine has evaporated, the concentration of mercury(II) chloride may become so high that some may be lost by evaporation. To keep the concentration low, to keep the mercury(II) chloride in solution, and to wash the walls of the container during the evaporation, some hydrochloric acid is added to the liquid chlorine before the evaporation is started. The hydrochloric acid concentration is rather critical, because at most concentrations, hydrochloric acid will be solid at −35 °C, the temperature of boiling chlorine at one atmosphere. When the acid concentration is near 8 M, no solidification will occur. After the evaporation of the chlorine, the hydrochloric acid may contain other compounds than mercury compounds, for example, iron(III) chloride and chlorinated organic compounds. Some of these chlorinated compounds are volatile and absorb u.v. radiation of 253.7 nm. To prevent interferences from these compounds, the hydrochloric acid is extracted with carbon tetrachloride. The mercury can then be determined in the hydrochloric acid as described previously [1]. In sampling gaseous chlorine, one of the methods given earlier for air [1] can be used to isolate the mercury from the large amount of chlorine.

Sampling of chlorine, liquid or gas, can give trouble because deposits on the walls of containers or pipes can be present, which may contain mercury(I) or (II) chloride. During sampling, some of these deposits may come loose and may be sampled with the chlorine, giving erroneously high analytical results. Moreover, when gaseous chlorine is sampled, solid particles may be present with mercury compounds adsorbed on it, or there may be aerosols of mercury chloride. This means that the mercury content of chlorine gas cannot be determined by the method with washing bottles filled with acid permanganate, but only by the bulb method [1].

Part of the method given below resembles the method used by the Dow Chemical Company [4].

DESCRIPTION OF METHOD*

Scope and field of application

This method is suitable for the routine determination of mercury in liquid and gaseous chlorine. The lower limit of detection is approximately 0.2 μg Hg kg^{-1} for liquid chlorine. For gaseous chlorine it is approximately 15 μg Hg Nm^{-3} if a 1-l sample of gas is used. A lower limit of detection can be obtained by using a larger volume of gas.

Principle

The liquid chlorine is introduced into a refrigerated trap containing hydrochloric acid (8 M). It is then slowly evaporated at atmospheric pressure. The mercury remains in the residue. Organic substances which remain in the residue on evaporation are removed by washing with carbon tetrachloride. It is necessary to confirm that this does not cause extraction of mercury from the sample; this can be done by a separate analysis of the extract with a Wickbold burner [2], for example. The mercury in the aqueous phase is finally determined by flameless atomic absorption spectrometry.

Gaseous chlorine is sampled in a bulb as described for gases [1].

Apparatus and reagents

An atomic absorption spectrophotometer and accessories, and reagents, are used as described previously [1].

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*For technical reasons, the text of the method has been modified and shortened in certain places; those interested in the original text can obtain it in French, German or English, on application to the BITC.

The liquid chlorine sample cylinder is made of special steel (e.g. 18/8) resistant to chlorine, nitric acid (7 M) and to pressure; the diameter is about 100 mm, and the length about 350 mm. The cylinder is fitted at each end with a nickel valve with a stainless steel spindle. This cylinder is subject to the pressure vessel regulations. An example of a suitable cylinder is shown in Fig. 1.

Other equipment includes a glass wash bottle (about 500 ml capacity), separating funnels (capacity 250 ml and 500 ml), and a bulb (volume ⩾ 1000 ml) with two PTFE-taps as described previously [1].

Hydrochloric acid, brominated. To 250 ml of hydrochloric acid (1 M), add 5 drops of bromine and mix. Store in a bottle with a ground-glass stopper.

Carbon tetrachloride. Purification with brominated hydrochloric acid is necessary to remove any interfering substances. To a 500-ml separating funnel add 100 ml of carbon tetrachloride and 100 ml of brominated hydrochloric acid. Shake vigorously for at least 2 min. Allow the layers to separate, run off the carbon tetrachloride and discard the aqueous phase. Replace the carbon tetrachloride in the separating funnel and carry out a

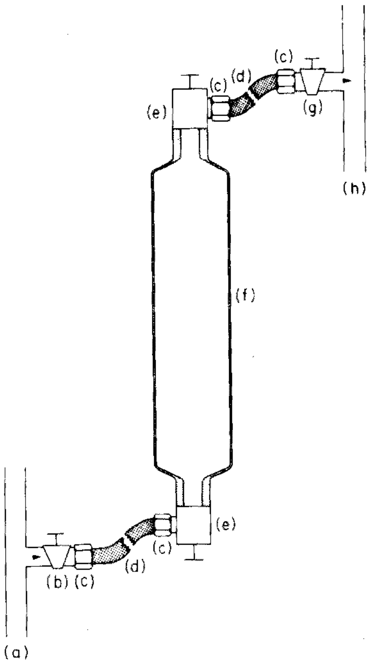

Fig. 1. Liquid chlorine sample cylinder. (a) Liquid chlorine main. (b) Isolation valve. (c) Threaded connection for the flexible pipe to the sample cylinder. (d) Chlorine-resistant flexible pipe (e.g. in copper). (e) Special steel needle valve. (f) Special steel cylinder suitable for working under pressure. (g) Vent main isolation valve. (h) Vent main.

second extraction. Allow the layers to separate and transfer the carbon tetrachloride to a suitable brown glass bottle.

Procedure for liquid chlorine

Sample collection. It is advisable to provide a sampling point for liquid chlorine on the plant installed in a cupboard (see Fig. 1). This point should consist of a sample valve in special steel fitted with a suitable connection to allow it to be attached to the lower valve of the sample cylinder. The upper valve should be connected to a vent main by means of a flexible tube.

For each sample two cylinders are necessary, the first serving as a purge for the sample circuit. Before taking the sample, rinse the steel cylinders with nitric acid (7 M) followed by water and then with alcohol, and dry them.

Connect the lower valve of the first cylinder to the sample point on the chlorine main. Connect the upper valve to the vent main. Open the valves so that the liquid chlorine slowly enters the cylinder. The amount which has entered may be judged from the layer of frost which forms slowly on the outside of the cylinder. Close the sample valve and then the cylinder valves, and disconnect them. Discard the first sample since it may contain mercury chloride residues deposited in the pipes. Depending on the design of the installation, this sample may be reintroduced further on in the chlorine circuit by means of the vent tube. Connect the second cylinder and proceed to collect the actual samples as described above. For safety reasons, it is important that this cylinder should be no more than half full (about 2.5 kg of chlorine).

Sample preparation and mercury determination. Carefully rinse the wash bottle with nitric acid (7 M) and then with water. Introduce into it 3 ml of hydrochloric acid (8 M) and place it in a refrigerant bath of methylene chloride and solid carbon dioxide (temperature less than $-60\,^{\circ}C$). Weigh the chlorine cylinder and then allow about 500 g of liquid chlorine to flow into the wash bottle. Reweigh the cylinder; the difference in weight represents the chlorine sample weight (W kg). Remove the wash bottle from the refrigerant bath and allow the chlorine to evaporate slowly at atmospheric pressure, absorbing the gas in 3.5 l of sodium hydroxide solution (6 M) via a guard flask (theoretically, this can absorb 700 g of chlorine). To avoid losses of mercury, ensure that the evaporation is steady and slow enough to take at least 4 h.

After evaporation of the chlorine, introduce 40 ml of brominated hydrochloric acid into the chlorine wash bottle, and swirl the bottle so that all the inner surface is washed by the acid. Transfer the solution to a 250-ml separating funnel. Introduce 40 ml of purified carbon tetrachloride to the wash bottle to dissolve any organic residues which may be present; transfer this solution to the separating funnel. Rinse the wash bottle with 40 ml of brominated hydrochloric acid, and add this solution also to the separating funnel. Shake the contents of the separating funnel for 2 min. Allow the layers to separate, run off the organic phase and discard it. Collect the hydrochloric acid solution in a 100-ml standard flask. Dilute to volume and mix. Take an aliquot of this solution (V ml) and place it in a 100-ml beaker provided with a cover glass. Add successively 1 ml of sulphuric acid (1+4) and 1 ml of potassium permanganate solution (40 g l^{-1}). Heat and boil for a few seconds; cool. Reduce the excess of potassium permanganate by the dropwise addition of hydroxyammonium chloride solution (100 g l^{-1}). Transfer the solution to an aeration flask and measure the mercury content by the procedure given under 'Determination of mercury content' in Part I [1], taking into account the high chloride concentration (the standardization has to be done with solutions of the same concentrations of hydrochloric acid).

Carry out a blank determination with the same quantities of all the reagents used in the analysis.

Calculation. Hg μg kg^{-1} $= \frac{(C - C_o) \times 100}{W \cdot V}$

where $C = \mu$g Hg from calibration curve; $C_o = \mu$g Hg in blank; W = sample weight (kg); V = volume of the aliquot taken from the standard flask (ml).

Procedure for gaseous chlorine

The procedure is given in Part I [1] under 'Sample preparation for hydrogen and air; Higher mercury content (more than 5× the limit of detection per litre of sample)'. Great care is necessary during sampling. It is particularly important to ensure that any entrainment of solid particles (calomel and sublimate) from the chlorine main line into the sample bulb is avoided. To obtain a lower limit of detection, a bulb with a volume greater than 1 l can be used and/or the sampling procedure can be repeated more than once with the same absorbing solution.

Calculation. Hg mg m^{-3} $= \frac{250 \cdot (C - C_o)}{n \cdot q \cdot V}$

where $C = \mu$g Hg from calibration curve; $C_o = \mu$g Hg in blank; n = number of samples taken in the bulb; q = volume of aliquot analysed (ml); V = volume of the bulb (l).

TESTING THE METHODS

For practical reasons, it was not possible to test the methods with interlaboratory tests. Therefore, the laboratories that participate in the Bureau International Technique du Chlore tested the methods with their own product. Furthermore, the most critical parts of the methods, the sample pretreatments, were thoroughly tested. The results are discussed below.

Method for liquid chlorine

Many tests were done to check if mercury is lost during the evaporation of the liquid chlorine. (a) Mercury(II) chloride was added to liquid chlorine. After evaporation of the chlorine, all the added mercury was found in the hydrochloric acid (see Table 1). (b) Gaseous chlorine from evaporating liquid chlorine was led through wash bottles which contained acid permanganate solution [1]. The formation of aerosols containing mercury is very improbable under these circumstances. No mercury was found in this permanganate (work done by members of the Chlorine Institute, New York). Also the gaseous chlorine was recondensed and evaporated again. No mercury could be detected in the recondensed sample, which means that at least 99 % of the mercury was found in the first determination.
(c) Radioactive mercury(II) chloride was added to the liquid chlorine before evaporation. If the chlorine was allowed to boil smoothly, 95—103 % recovery of mercury in the hydrochloric acid was obtained. Irregular boiling of the sample caused the recovery to drop to 86—92 % (see Table 1).
(d) Sodium hydroxide, used for the absorption of the evaporating chlorine, was analyzed for mercury before and after the evaporation of the chlorine. No significant increase in mercury content could be found. (This determination must be done with great care because of the large amount of sodium hydroxide necessary for the absorption of all the chlorine and the low mercury concentration of the chlorine compared to that of ordinary sodium hydroxide. Furthermore, the mercury content of sodium hydroxide decreases with time, so that the blank is changing too. As work done by the members of the Chlorine Institute, New York, has demonstrated, there is a severe and variable interference from an unknown component, that also absorbs at 253.7 nm. That this absorption is due to non-atomic absorption can be seen from the simultaneous absorption at 248.3 nm, an iron line. The formation of this interfering compound can be avoided by doing the final reduction of the mercury with sodium stannite solution at high pH instead of tin(II) chloride.)

TABLE 1

Recovery of mercury added as $HgCl_2$ to liquid chlorine

Exp.	Hg added (μg kg^{-1})	Recovery (%)	Remarks	Method of determination
1	20	97		As given in this paper
2	50	103		
3	10	98		
4	13.8	95	Smooth boiling	With radioactive ^{203}Hg
5	13.8	103		
6	1.38	87	Irregular boiling	
7	1.38	86		
8	1.38	92		
9	1.38	100	Smooth boiling	

Tests were also made to check that $HgCl_2$ was not lost in the extraction procedure with carbon tetrachloride. As can be seen from Table 2, no losses were found.

Method for gaseous chlorine; testing of both sampling methods given in Part I [1].

Because of the low mercury content of chlorine, much gas has to be sampled for an analysis. The most suitable method in this case is the absorption method, but because of the possibility of aerosols of mercury-chlorine compounds and mercury adsorbed on dust particles, this method was compared with the bulb method. The results are given in Table 3. From these experiments it is clear that the results for mercury in chlorine gas can be far too low when the absorption method is used. Therefore we recommend only the bulb method for this determination. This implies a limit of detection that is much higher than for the absorption method. This limit can be lowered by taking a bulb with a volume greater than 1 l and/or by repeating the sampling procedure several times.

TABLE 2

Recovery of mercury added as $HgCl_2$ to hydrochloric acid, after extraction with carbon tetrachloride
(40 ml of 1M HCl was used in all cases.)

Exp.	ml CCl_4	Hg added (μg)	Recovery (%)	Method of determination
1	20	0.5	97	As given in this paper
2	20	0.2	103	
3	20	0.02	96	
4	40	1.4	102[a]	With radioactive ^{203}Hg
5	40	0.14	101[a]	
6	40	0.14[b]	100[a]	

[a]No radioactivity in carbon tetrachloride. [b]+ 5 g of chlorinated organic residue of chlorine plant.

TABLE 3

Analysis of wet chlorine gas by the absorption method (Results are given as percentages of the mercury contents determined by the bulb method.)

Exp.	Wash bottles (placed in series) filled with					
	HCl	HCl	$KMnO_4$	$KMnO_4$	$KMnO_4$	HCl + CCl_4
1	1.5	1.1	1.2	1.3	0.4	—
2	16	—	—	—	—	—
3	—	—	—	—	—	5.2
4	—	—	21	—	—	—

REFERENCES

1 Mercury Analysis Working Party of BITC, Anal. Chim. Acta, 72 (1974) 37.
2 Mercury Analysis Working Party of BITC, Anal. Chim. Acta, 84 (1976) 231.
3 Edward W. Washburn (Ed.), International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. III, McGraw-Hill, New York, 1928, pp. 206—214.
4 Determination of Mercury by Atomic Absorption Spectrometry. Method No. CAS-AM-70.13, The Dow Chemical Company, Midland, Mich., U.S.A.

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THE DETERMINATION OF CADMIUM IN PLANT MATERIAL AND SOIL EXTRACTS BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION WITH A CARBON-ROD ATOMIZER

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SUMMARY

A method is described for the determination of cadmium in plant materials and acetic acid extracts of soils. Cadmium is collected from aqueous solutions by dithizone-in-chloroform solvent extraction and determined by atomic absorption spectrometry with a carbon-rod atomizer. A detection limit of 0.001 p.p.m., in the aqueous solution, with a precision of ± 3—4% is obtained. Interference effects are negligible and the method has been in routine use for over two years.

Cadmium has been determined successfully by conventional flame atomic absorption methods in soil extracts [1—6] and fertilizers [7, 8] without prior separation. These techniques have, in our experience, proved inadequate for low levels of cadmium in soils unless correction is made for the non-specific light-loss effects from major elements such as calcium, or a separation technique employed [5, 9, 10]. Similar findings have been reported for fertilizers [7] and urine [9]. With sample solutions of ashed plant materials, in which cadmium concentrations are usually lower and major element concentrations are higher than in soil extracts, a separation procedure is almost essential [11]. The present paper describes the determination of cadmium in solutions of ashed plant material and extracts of soil, after dithizone-in-chloroform solvent extraction, by atomic absorption spectrometry with a carbon-rod atomizer [12, 13].

Preliminary considerations

The practical limit of determination for cadmium in solution by flame methods is about 0.01 p.p.m. As the maximum salt content for effective nebulization of plant ash solutions is about 1 %, the maximum dry plant-to-solution weight ratio is about 1:10. The limit of determination for cadmium in plant material by flame methods is therefore only about 0.1 p.p.m. In addition, matrix interference as a result of non-atomic absorption, and light-scattering loss arising particularly from the high concentrations of calcium, aluminium, iron, sodium, magnesium and potassium [5], can provide interfering signals equivalent to an apparent plant cadmium concentration of up to 0.5 p.p.m. Even when a background correction [14] method is used, the accuracy of the determination is poor.

The carbon-rod atomizer has a sensitivity at least ten times that of the flame, but this apparent advantage was illusory in practice for two reasons: first, the precision for aqueous solutions of high salt content was, in our experience and that of others [10, 15], unacceptably low; secondly, the high concentrations of matrix elements not only gave rise to positive interference effects but also drastically inhibited the evolution of monatomic cadmium vapour, as has been noted for cadmium [10] and other elements such as cobalt in soil extracts [15].

A prior separation of cadmium is therefore essential for the analysis of plant ash solutions by both flame and carbon-rod atomization. Solvent extraction procedures with APDC in MIBK [16—18], NDDC in MIBK [19] and from iodide into MIBK [20] have been applied to the flame atomic absorption determination of cadmium. Dithizone extraction techniques, originally applied for the colorimetric determination of cadmium [21—23], have been adapted to flame atomic absorption analysis [8] and for the carbon furnace atomizer [24, 25]. Dithizone-in-chloroform extraction followed by direct aspiration of the chloroform phase into the flame is dangerous because of the toxic combustion products. Dithizone-in-chloroform extracts have therefore been applied directly to a carbon-rod atomizer for determination by atomic absorption.

EXPERIMENTAL

Sample preparation

Plant material. Finely-milled, oven-dried (80 °C) plant material was ashed overnight in silica or platinum at 450 °C. Ash, equivalent to about 1 g of oven dry material, was twice taken to dryness with 5 ml of 6 M redistilled hydrochloric acid; the residue was treated with 10 ml of 0.06 M hydrochloric acid and the filtrate was used for solvent extraction.

Acetic acid extracts of soils. Air-dried soil (20 g; < 2 mm) was extracted overnight with 800 ml of 0.5 M acetic acid, filtered, and taken to dryness on a steam bath. The residue, taken to dryness twice with 5 ml of redistilled nitric acid (67—68 %, w/w) and once with 10 ml of 6 M hydrochloric acid, was dissolved in 10 ml of 0.06 M hydrochloric acid, and filtered. This solution could be aspirated directly into an air—acetylene flame for conventional atomic absorption determination, or atomized with a carbon-rod after dithizone-in-chloroform extraction.

Standard solutions

From a stock solution containing 1000 p.p.m. cadmium [prepared either from cadmium oxide (ignited at 600 °C) in dilute hydrochloric acid or from AnalaR cadmium sulphate, $3\ CdSO_4 \cdot 8\ H_2O$ in distilled water] solutions containing 100 p.p.m. and 10 p.p.m. were prepared in 0.06 M hydrochloric acid. Standard solutions in 0.06 M hydrochloric acid, containing 0.01, 0.05, 0.1, 0.2 and 0.3 p.p.m. cadmium were prepared from these. As a precaution against adsorption losses in borosilicate glass vessels the standard solutions were not kept for more than a few days. The standard solutions and a blank were included with each batch of samples analyzed; all the solutions were treated by solvent extraction.

Solvent extraction procedure

Although dithizone-in-chloroform extraction schemes, which minimize the extraction of copper or zinc, have been used [21] for the colorimetric determination of cadmium, the method described was based on a simpler procedure [26] in view of the specificity of the atomic absorption measurement.

A 5-ml aliquot of sample or standard solution was pipetted into a 30-ml pyrex ground-glass stoppered test-tube, 4 ml of ammonium citrate (400 g l^{-1}) solution was added and the pH was adjusted to 8—9 with ammonia (phenol red indicator). Freshly prepared 0.05 % dithizone-in-chloroform solution (2 ml) was added, and the stoppered tube was shaken mechanically for 5 min. The organic phase was collected by filtration through a Whatman PS 1 phase-sensitive filter paper. The aqueous phase in the filter paper was transferred to the test tube, and re-extracted with 2 ml of dithizone-in-chloroform solution, and the organic phase was separated by filtration and added to the first extract for analysis. Extractions of about 20 samples per hour can be made. This extraction technique was quantitative for up to at least 0.5 p.p.m. cadmium in the original aqueous solutions. A sufficient excess of the dithizone reagent is indicated by the green colour of the chloroform extract. Where high concentrations of cadmium or certain interfering elements are present (see "Interference Effects"), 0.2 % dithizone-in-chloroform solution can be used with advantage.

Apparatus

The atomic absorption determinations were made with a laboratory-built, multi-element, atomic absorption and fluorescence spectrometer incorporating a carbon-rod atomizer [12] similar to that of Alder and West [13]. The easily-machined form of the rod is shown in Fig. 1. The rod was heated by a

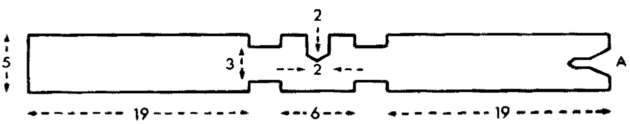

Fig. 1. Diagram of the carbon-rod used in the atomizer; dimensions in mm. A Centre-drilled hole for machining in a lathe.

12 V transformer rated continuously at 100 A and controlled by a manually operated variable transformer (7 A, 240 V) with provision for measuring the current. The rod was protected from oxidation by an upward flow of argon at 3 l min^{-1}. Both graphite and carbon have been used successfully but rods made from 5.5 mm diameter spectrographic carbon (Morganite, Grade SG-905-J) were preferred to those from graphite since their lower thermal conductivity produced less heating of the water-cooled, stainless-steel, terminal blocks (F, G, Fig. 2) and, therefore, a shorter cooling time between sample insertions (about 2 min). An inexpensive Hilger and Watts D292 grating monochromator, C, (slit width 0.05 mm), an unmodulated cadmium hollow-cathode lamp, J, and an EMI 9660B photomultiplier tube, B, were employed with simple two-lens (D, E, fused silica) optics. Voltage signals developed in the photomultiplier load (100 K resistor in parallel with a 0.022 μF capacitor) supplied a pen recorder, A, (Servoscribe RE541.20, response time about 0.5 s) or alternatively a digital voltmeter with a peak-reading facility (Dynamco Type DM 2001 Mk 2). Although the latter had a faster response (0.04 s) than the recorder and thus avoided the slight truncation of the absorption peaks obtained with the recorder, the recorder was preferred because the time sequence of events, from sample insertion to atomization, could be followed more easily and no loss in precision was found with recorder output. An alternative hydrogen-lamp source, K, was incorporated to ensure that background correction for molecular absorption or light scattering interference effects could be carried out. In practice such effects were negligible and this facility was not used.

Operation

The carbon-rod was cleaned by preheating in the apparatus until no absorption was observed. A 5-μl aliquot of a dithizone-in-chloroform extract was pipetted into the sample-well of the rod with a glass capillary-tube micropipette (Drummond Microcap; Shandon Southern Instruments Ltd.). After drying by heating for 1 min at 6 A the extract was ashed for 1 min

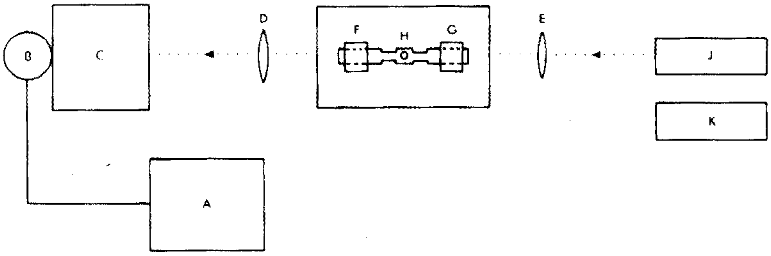

Fig. 2. Schematic diagram of the atomic absorption apparatus with carbon-rod atomizer. A, Pen-recorder. B, Photomultiplier tube. C, Monochromator. D, E, Fused Silica Lenses. F, G, Water-cooled terminal blocks. H, Carbon rod. J. Cadmium hollow-cathode lamp. K, Hydrogen lamp.

at 10 A to destroy the organic material, and the cadmium was atomized by increasing the current to 90 A until the absorption peak was recorded. The current was then reduced to zero and the rod was allowed to cool for 2 min before inserting the next sample and repeating the procedure. The pipetting operation requires skill; to ensure that it had been carried out correctly, a second 5-μl aliquot of the sample was used. If the first absorption peak was not reproduced to within 1 or 2 % of the recorder full-scale deflection, a third determination was made and the discordant measurement was discarded. The results were calculated from a calibration curve of concentration versus absorbance, which was linear up to about 0.2 p.p.m. with slight curvature from 0.2 to 0.3 p.p.m.

Interference effects

No effect on the cadmium absorbance was found when the original aqueous solutions before extraction contained a maximum of 5000 p.p.m. of calcium, 1500 p.p.m. of potassium, 1000 p.p.m. of magnesium or 500 p.p.m. of aluminium, chromium, iron, lead, manganese, phosphorus, or sodium. Interference was not experienced when solutions contained a combined matrix of 750 p.p.m. of calcium, 900 p.p.m. of magnesium, 1200 p.p.m. of potassium, 400 p.p.m. of phosphorus and 300 p.p.m. of sodium.

A depressive interference was given by high concentrations of phosphorus, e.g. 10 % at 1000 p.p.m. and 40 % at 5000 p.p.m. of phosphorus, but this should seldom cause problems with plant sample solutions, which usually contain less than 1000 p.p.m. of phosphorus.

High concentrations of zinc and copper depress cadmium, probably as a result of competition for the dithizone reagent, but as pH 8—9 was used throughout, the extraction of zinc was minimized. With 0.05 % dithizone in chloroform, interference was not caused by copper in concentrations less than 25 p.p.m. nor by zinc in concentrations less than 250 p.p.m. in the aqueous sample solution. The contents of these elements in most normal plant materials should not present problems, but if these levels are likely to be exceeded, increasing the dithizone concentration to 0.2 % gives freedom from depression by up to 100 p.p.m. of copper or 1000 p.p.m. of zinc or by a combination of 50 p.p.m. of copper and 500 p.p.m. of zinc. A preliminary dithizone-in-chloroform extraction at pH 2 can also be used to reduce exceptionally high copper concentrations to manageable proportions.

RESULTS AND DISCUSSION

While wet digestion [1, 3, 26] and bomb (dissolution) methods [27] have been used for the dissolution of organic samples before the determination of cadmium, dry ashing [11] at 450 °C was selected initially because of its simplicity and freedom from contamination. As low temperature ashing in excited oxygen [28] has been used to avoid the possibility of volatilization losses, the recovery of cadmium, added as $CdCl_2$ to a variety of plant materials before ashing, was investigated. Table 1 shows this to be within ± 10 % for most samples, with an overall average recovery of 95.9 %. The exceptional, low recovery in two of the samples is the subject of a further investigation to establish whether volatilization losses, sampling errors, or interference effects are involved. As these results include all other sources of error, as well as the effects of losses by volatilization, the latter does not appear to be a major source of error for most types of plant material analyzed. A similar conclusion has been reached for soils ignited at 475 °C [20].

The precision of the atomic absorption measurement, measured by analyzing ten replicate standard solutions, ranged from s_r = 3.04 % to 3.96 % for 0.1 p.p.m. and 0.5 p.p.m. concentrations, respectively. The reproducibility of the complete procedure, including sub-sampling the milled plant material, over a period of six months is shown in Table 2 and does not exceed ± 0.015 p.p.m.

The accuracy of the method, illustrated (Table 1) in terms of the recovery of added cadmium, was also investigated by comparative analysis of plant

TABLE 1

Recovery of 1.0 p.p.m. of cadmium added as $CdCl_2$ to different plant materials before ashing at 450 °C

Plant material	Original Cd content p.p.m. (Oven-dried)	Recovery of added Cd %	Plant material	Original Cd content p.p.m. (Oven-dried)	Recovery added Cd %
Oat grain A	0.11	114	Mixed herbage	<0.01	87
Oat grain B	0.11	99	Red clover	0.02	76
Oat straw	0.06	105	Potato shaws	1.09	95
Barley grain	<0.01	106	Potato tuber	0.20	94
Barley straw	<0.01	112	Turnip shaws	0.19	96
Wheat grain	0.08	90	Turnip root	0.07	97
Wheat straw	0.09	70	Kale tops	0.23	100
Ryegrass	0.03	97	Sugar beet	0.22	97
		Mean recovery 95.9 %			

TABLE 2

Reproducibility of five replicate analyses of plant material at intervals over a period of six months

Sample	Cd, p.p.m.						s	s_r (%)
	1	2	3	4	5	Mean		
Ryegrass	0.05	0.05	0.03	0.03	0.03	0.038	± 0.011	28.9
Oat grain	0.09	0.12	0.09	0.12	0.11	0.106	± 0.015	14.2
Kale tops	0.25	0.23	0.22	0.24	0.23	0.234	± 0.014	5.9

material by this method and by anodic stripping voltammetry. Good agreement was obtained by the two methods for plant material contents of about 1 p.p.m. of cadmium; a mean value of 1.10 p.p.m. was found compared with 1.26 p.p.m. by anodic stripping voltammetry. At 0.1 p.p.m. the present method gave slightly but significantly higher values.

Further comparisons were made by analyzing acetic acid extracts of soils by the present method and by flame atomic absorption without any solvent extraction (Table 3); allowing for the poorer sensitivity of the flame method, the agreement is generally good.

Repeated analysis of U.S. National Bureau of Standards Orchard Leaves, S.R.M. 1571, with an authenticated cadmium content of 0.11 ± 0.02 p.p.m. gave a value of 0.16 ± 0.016 p.p.m. With a hydrogen lamp for background correction, it was shown that this higher value was not the result of molecular absorption or light-scattering losses. Atomic absorption analysis of the original aqueous solution of S.R.M. 1571 by graphite furnace atomizer with automatic background correction provided a value of 0.19 p.p.m., in reasonable agreement with the value found by the present method. A potato leaf sample gave similar contents of 1.15 (present method) and 1.10 p.p.m. (graphite furnace method).

Wheat flour, V-2/1, and dried potato, V-4, samples distributed for inter-laboratory comparative analysis by the International Atomic Energy Agency, Vienna, were found to contain 0.11 p.p.m. and 0.29 p.p.m., respectively. These values are in reasonable agreement with the quoted preliminary tentative values of 0.08 p.p.m. for V-2/1 (median value only) and a mean content of 0.227 ± 0.044 for V-4.

The method has been applied to a wide range of plants, soil extracts, and miscellaneous materials, such as fish meal. No problems have arisen in 2 years of routine operation. The method has high precision (±3—4 %), good sensitivity, and a detection limit of about 0.001 p.p.m. in aqueous solution, is almost entirely free from specific interference effects, and shows no evidence of interferences caused by molecular absorption or light scattering effects.

TABLE 3

Comparative analysis by atomic absorption of acetic acid soil extracts with (A) the carbon rod atomizer and solvent extraction procedure, and (B) the air-acetylene flame, without solvent extraction

Sample	Cd, p.p.m.		Sample	Cd, p.p.m.	
	A	B		A	B
1	0.09	0.12	7	0.24	0.26
2	0.05	0.05	8	0.13	0.20
3	0.09	0.11	9	0.03	<0.05
4	0.10	0.10	10	0.03	<0.05
5	0.10	0.19	11	0.22	0.21
6	0.11	0.14	12	0.14	0.13

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REFERENCES

1 H. L. Kahn, F. J. Fernandez and S. Slavin, At. Absorpt. Newslett., 11 (1972) 42.
2 M. K. John, G. J. Van Laerhoven and H. H. Church, Environ. Sci. Technol., 6 (1972) 1005.
3 A. Burkitt, P. Lester and C. Nickless, Nature (London), 238 (1972) 327.
4 F. Beavington, Aust. J. Soil Res., 11 (1973) 27.
5 S. Yamasaki, Nippon Dojo-Hiryogaku Zasshi, 44 (1973) 383.
6 Annual Report No. 43, Macaulay Institute for Soil Research, 1972—73, p. 33.
7 E. Miwa and F. Yamazoe, Soil Sci. Plant Nutr. Tokyo, 17 (1971) 141.
8 C. H. Williams, D. J. David and O. Iismaa, Commun. Soil Sci. Plant Anal., 3 (1972) 399.
9 J. B. Willis, Anal. Chem., 34 (1962) 614.
10 M. J. Dudas, At. Absorpt. Newslett., 13 (1974) 109.
11 M. Kushizaki and H. Komota, Nippon Dojo-Hiryogaku Zasshi, 41 (1970) 246.
12 T. S. West and X. K. Williams, Anal. Chim. Acta, 45 (1969) 27.
13 J. F. Alder and T. S. West, Anal. Chim. Acta, 51 (1970) 365.
14 T. C. Rains, M. S. Epstein and O. Menis, Vol. 3 of Acta 17th Colloq. Int. Spectrosc., Florence, 1973, p. 101.
15 A. C. Oborne, Filament Atomisers and their Application to Soil Analysis, Imperial College, London, PhD. Thesis, 1973.
16 N. Yamagata and I. Shigematsu, Bull. Inst. of Pub. Health, Tokyo, 19 (1971) 1.
17 T. Kono and S. Kobayashi, Bunseki Kagaku, 19 (1970) 1491.
18 T. Takijima and F. Katsumi, Soil Sci. Plant Nutr. Tokyo, 19 (1973) 29.
19 E. Berman, At. Absorpt. Newslett., 6 (1967) 57.
20 R. M. Dagnall, T. S. West and P. Young, Talanta, 13 (1966) 803.
21 B. E. Saltzman, Anal. Chem., 25 (1953) 493.
22 F. D. Snell and C. T. Snell, Colorimetric Methods of Analysis, Vol. 2, Van Nostrand, New York, 3rd edn., 1955, p. 144.
23 E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd edn., Interscience, New York, 1959, p. 353.
24 J. Aggett and T. S. West, Anal. Chim. Acta, 57 (1971) 15.
25 Y. Yamamoto, T. Kumamaru, T. Kamada, T. Yanada and M. Kawabe, Nippon Kagaku Kaishi, No. 5 (1975) 836.
26 Analytical Methods Committee, Analyst (London), 94 (1969) 1153.
27 P. E. Paus, At. Absorpt. Newslett., 11 (1972) 129.
28 R. Tanaka, M. Yada and T. Kobayashi, Shokuhin Eiseigaku Zasshi, 11 (1970) 84.

Analytica Chimica Acta, 87 (1976) 291—300

NOUVELLE MÉTHODE DE MESURE RAPIDE DE TRÈS FAIBLES CONCENTRATIONS D'ATOMES D'HYDROGÈNE DANS UN ÉCOULEMENT GAZEUX

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RÉSUMÉ

Le présent article décrit une nouvelle méthode destinée à détecter la présence d'hydrogène atomique dans un réacteur ouvert jusqu'à des concentrations de l'ordre de $5 \cdot 10^{-10}$ M. Les atomes réagissent sur une surface d'oxyde de mercure(II) en libérant du mercure dont on mesure la concentration en continu par spectrophotométrie à 253.7 nm. D'une mise en oeuvre très simple et peu onéreuse, cette méthode présente des performances comparables à celles des méthodes habituelles souvent plus sophistiquées.

SUMMARY

A new method is described for the determination of atomic hydrogen in concentrations as low as $5 \cdot 10^{-10}$ M in flow systems. The atoms react on a mercury(II) oxide target and liberate mercury, the concentration of which is measured by spectrophotometric absorption at 253.7 nm. Because of its simplicity and low cost, the method compares very favourably with more sophisticated techniques.

Plusieurs techniques sont actuellement utilisées pour détecter la présence d'atomes d'hydrogène dans un milieu réactionnel [1, 2]. Les plus courantes sont: (a) les techniques de RPE de plus en plus utilisées pour leur sensibilité et leur sélectivité, mais l'appareillage ne présente pas toujours une grande souplesse d'emploi; (b) les techniques basées sur l'absorption de la raie Lyman α (121.578 nm) fort séduisantes par leur finesse et leur sélectivité mais de mise en oeuvre assez délicate; et (c) les méthodes de chimiluminescence qui permettent des dosages quantitatifs. Fondées sur la mesure de l'émission de molécules HNO* elles nécessitent l'introduction volontaire de monoxyde d'azote dans le milieu réactionnel.

Le présent article a pour objet la description d'une nouvelle méthode, de nature chimique dont les principaux avantages sont la sensibilité et la simplicité. Au voisinage de la température ambiante, l'hydrogène atomique présente la propriété de pouvoir réduire un grand nombre d'oxydes métalliques [3] dans des conditions où l'hydrogène moléculaire ne réagit pas. Le métal libéré reste sous forme solide sauf dans le cas de l'oxyde de mercure(II) HgO. En effet, dans l'hypothèse où la concentration en atomes est suffisamment faible, le mercure est libéré nettement en dessous de sa tension de vapeur saturante et apparaît ainsi sous forme gazeuse. Si cette réaction s'effectue en réacteur ouvert, la concentration en mercure peut alors être aisément mesurée en aval et de façon continue par spectrophotométrie à 253.7 nm, une technique dont la grande sensibilité est bien connue.

Le signal délivré par le spectrophotomètre ne sera représentatif de la concentration incidente en hydrogène atomique qu'à la condition de connaître les lois qui relient d'une part la concentration en atomes à la concentration en mercure, et d'autre part la concentration en mercure au signal obtenu.

PARTIE EXPÉRIMENTALE

Une sonde recouverte d'oxyde de mercure(II) intercepte un courant gazeux contenant des atomes d'hydrogène qui réagissent lors du contact avec HgO. Le mercure libéré en phase vapeur est transporté en aval par le gaz jusqu'à une cellule où sa concentration est mesurée par spectrophotométrie.

La sonde

Il convient de préciser d'abord la nature de l'oxyde utilisé, son mode de dépôt sur le support et la forme géométrique de ce dernier. Il existe deux variétés de HgO [4] : la forme jaune présente une réactivité nettement plus grande vis à vis des atomes d'hydrogène. Les deux variétés utilisées sont des produits RP ("Pour Analyse", Prolabo).

Le problème du mode de dépôt de l'oxyde sur la sonde peut être très simplement résolu en préparant une bouillie aqueuse que l'on dépose à l'aide d'un pinceau sur le support en "pyrex". Ce dépôt est ensuite séché dans un courant d'air. Sensible à tout choc mécanique, il s'avère cependant encore très bien resistant lorsqu'il est exposé à des vitesses de gaz pouvant atteindre 4 ms^{-1}. Ce support constitue en lui-même un véritable petit réacteur dont la forme géometrique peut avoir une grande influence sur le rendement en mercure libéré et sur la loi reliant la concentration en atomes d'hydrogène recherchée à celle de la vapeur de mercure recueillie. Deux formes ont été étudiées et utilisées avec succès: la grille et le tube.

Dans le premier cas, l'oxyde est déposé sur une grille en pyrex (mailles d'environ 1 mm^2) à travers laquelle circule le gaz (Fig. 1). Les atomes parviennent sur la surface active grâce à la turbulence créée au moment du contact avec l'obstacle constitué par la grille. Dans le second cas, l'oxyde est déposé sur la paroi intérieure d'un petit tube cylindrique en pyrex (Fig. 1). Le gaz s'écoule à l'intérieur en régime laminaire et les atomes n'atteignent l'oxyde que par diffusion moléculaire.

Analyse de la concentration en mercure

La mesure repose sur l'analyse spectrophotométrique de l'absorption par le mercure de la raie 253.7 nm [5, 6].

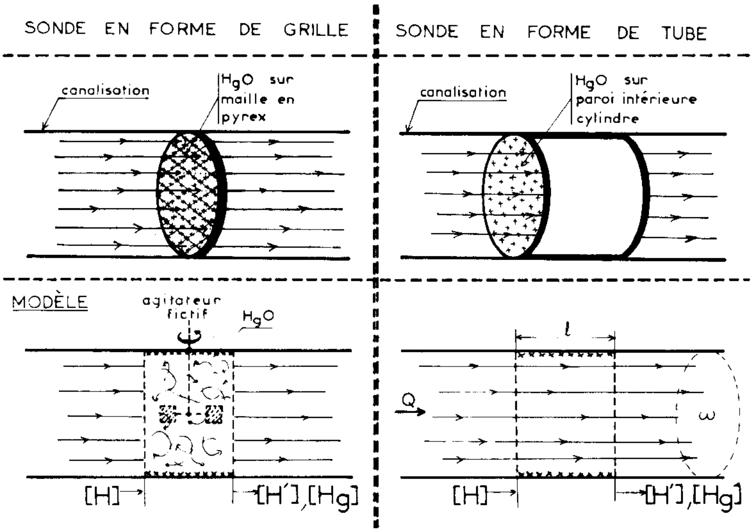

Fig. 1. Représentation schématique de deux géométries de sondes à oxyde mercure(II).

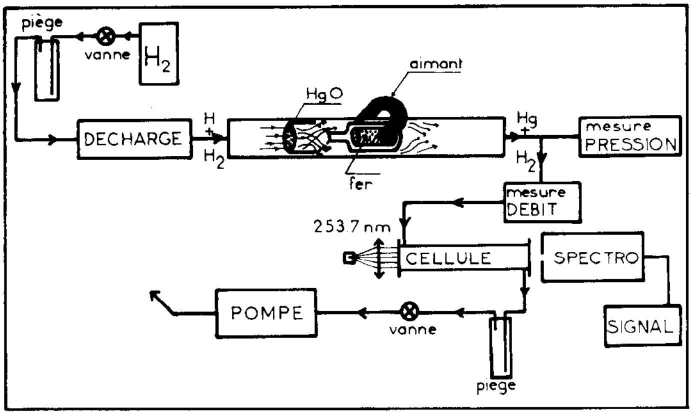

Fig. 2. Schéma de principe du montage expérimental destiné à tester les performances de la sonde à oxyde mercure(II).

En aval de la sonde, le gaz contenant la vapeur de mercure traverse en continu une cellule constituée par un tube cylindrique en pyrex (longueur 0.5 m) délimité à ses deux extrémité par deux fenêtres en quartz parallèles (Fig. 2). Le gaz intercepte un faisceau de rayonnement 253.7 nm émis par une lampe à vapeur de mercure basse pression. L'intensité résiduelle non absorbée est détectée à l'aide d'un spectrophotomètre dont le signal est analysé en continu sur un enregistreur. De très bons résultats ont été également obtenus en remplaçant le spectrophotomètre par un photomultiplicateur du type solar-blind (RTC).

Montage destine à tester les performances de la méthode

Le montage est schématisé sur la Fig. 2.

Un courant d'hydrogène (de qualité "U" de l'"Air Liquide") très faiblement dissocié par décharge Corona circule en régime permanent et isotherme dans un réacteur cylindrique en pyrex (section 1.45 cm^2). Grâce à un système d'aimant agissant de l'extérieur, la sonde peut être aisément positionnée aux abscisses désirées, ce qui autorise ainsi l'exploration de zones où les concentrations atomiques sont différentes. Pression et débit peuvent être réglés à volonté grâce à l'ensemble constitué par une pompe pour vide primaire et deux vannes à aiguille.

PARTIE THEORIQUE

Nous supposerons qu'après la formation très rapide d'une couche chimisorbée sur l'oxyde, les atomes d'hydrogène incidents peuvent donner lieu soit à une réaction de recombinaison simple, soit à la formation de mercure.

$$\mathrm{H + HgO \xrightarrow{rapide} (HgO)H}$$

$$\mathrm{H + (HgO)H \xrightarrow{\mathit{k}_1} H_2 + HgO}$$

$$\mathrm{H + (HgO)H \xrightarrow{\mathit{k}_2} H_2O + Hg}$$

La sonde en forme de grille

On peut, en première approximation, représenter la sonde par un modèle où ce réacteur particulier serait assimilé à un mélangeur parfait continu dont la paroi intérieure serait recouverte d'oxyde sur une surface S identique à celle existant sur la grille (Fig. 1). Désignons par [H] et [H′] les concentrations des atomes à l'entrée et à la sortie du réacteur et par [Hg] la concentration du mercure en sortie. Par définition du mélangeur parfait, [H′] sera également la concentration, uniforme, régnant au sein du réacteur. La réaction entre l'oxyde et les atomes ne peut s'effectuer qu'après franchissement par ces derniers d'une couche limite. En désignant alors par $[\mathrm{H}]_s$ et $[\mathrm{Hg}]_s$ les concentrations régnant à la surface même du solide, on peut écrire les bilans de matière suivants

$$\text{pour H:}\quad \frac{Q}{s}[\mathrm{H}] = k_{\mathrm{H}}([\mathrm{H}'] - [\mathrm{H}]_s) + \frac{Q}{s}[\mathrm{H}']$$

$$\text{pour Hg:}\quad \frac{Q}{s}[\mathrm{Hg}] = k_{\mathrm{Hg}}([\mathrm{Hg}]_s - [\mathrm{Hg}])$$

où k_{H} et k_{Hg} sont les conductances de transfert de H et Hg à travers la couche limite et Q représente le débit volumique du gaz. Les flux de transfert étant reliés aux processus purement chimiques par les relations: $k_{\mathrm{H}}([\mathrm{H}'] - [\mathrm{H}]_s) = (k_1 + k_2)[\mathrm{H}]_s$, et $k_{\mathrm{Hg}}([\mathrm{Hg}]_s - [\mathrm{Hg}]) = 0.5\,(k_1 + k_2)[\mathrm{H}]_s$. On en déduit

$$\mathrm{Hg} = 0.5\,[\mathrm{H}] \Big/ \left(1 + \frac{Q}{s}\,\frac{k_1 + k_2 + k_\mathrm{H}}{(k_1 + k_2)\,k_\mathrm{H}}\right) \tag{1}$$

Cette expression, établie dans l'hypothèse où il n'y a pas accumulation de mercure au voisinage de l'oxyde, montre qu'il y a proportionalité entre la concentration en mercure recueillie et celle en atomes d'hydrogène incidente.

La sonde en forme de tube

Le gaz contenant les atomes traverse en régime d'écoulement laminaire (avec profil parabolique des vitesses) un tube cylindrique (de section ω) tapissé d'oxyde sur une longueur l (Fig. 1). Un tel réacteur tubulaire à parois catalytiques a fait l'objet d'une étude récente [7]. La concentration moyenne en réactif dans une section droite varie exponentiellement avec l'abscisse lorsque les processus chimiques sont d'ordre 1. Si [H] et [H′] sont les concentrations moyennes en atomes respectivement à l'entrée et en sortie de ce réacteur, on peut montrer que: $[\mathrm{H'}] = 0.82[\mathrm{H}]\ \exp(-l\omega/Q\tau)$, Q étant le débit volumique moyen du gaz. τ est une constante de temps représentative d'une part de la barrière diffusionelle que les atomes doivent vaincre pour parvenir à la surface et d'autre part des actes chimiques auxquels ils y donnent lieu

$$\tau = \frac{R^2}{3.66D} + \frac{R}{2(k_1 + k_2)} \tag{2}$$

R étant le rayon du réacteur, D le coefficient de diffusion moléculaire du réactif, et 3.66 une valeur numérique qui traduit le type d'écoulement (ici supposé laminaire).

Désignons par τ_2 une autre constante de temps représentative de la diffusion et du seul processus de formation de mercure telle que $\tau_2 = \tau$ quand $k_2 = k_1$ (éqn. 2). On peut facilement montrer que la concentration du mercure à la sortie du réacteur s'écrit alors

$$[\mathrm{Hg}] = 0.41\,\frac{\tau}{\tau_2}\left(1 - \exp\left(-\frac{l\omega}{Q\tau}\right)\right)[\mathrm{H}] \tag{3}$$

Ces relations supposent que la libération de mercure n'est pas contrôlée par sa vitesse d'évaporation.

L'intérêt de l'expression (3) est de montrer qu'avec ce type de sonde, il y a, ici encore, proportionalité entre la concentration en mercure recueillie et celle en atomes d'hydrogène incident.

Relation liant le signal delivre par le spectrophotomètre à la concentration en mercure

Cette loi peut être déterminée grâce à des expériences d'étalonnage réalisées grâce au montage annexe schématisé sur la Fig. 3. Dans une première phase, un courant principal d'hydrogène pur traverse la cellule (298 K et 1 atm): on

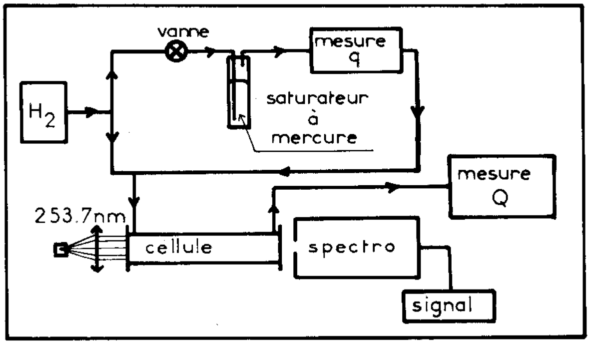

Fig. 3. Schéma du montage annexe destiné à effectuer les expériences d'étalonnage.

mesure une intensité lumineuse I_0. Dans une seconde phase, un courant secondaire (débit partiel q) saturé en mercure est mélangé au courant principal (débit total Q): on mesure alors une intensité I. Compte tenu de la valeur de la tension de vapeur saturante du mercure à 298 K ($2.43 \cdot 10^{-6}$ atm), la concentration en mercure régnant dans la cellule vaut: $[\mathrm{Hg}] = 10^{-7}\, q/Q$ ($\mathrm{mol\ l^{-1}}$). Posons $Si = L_n\, I_0/I$. Les resultats montrent que Si est une fonction linéaire de [Hg] dans la gamme de concentrations $2 \cdot 10^{-10}$—$4 \cdot 10^{-9}$ $\mathrm{mol\ l^{-1}}$ et permet de calculer

$$Si = 3.55 \cdot 10^{8}\ [\mathrm{Hg}] \qquad (4)$$

Cette constatation expérimentale indique que, dans nos conditions, la loi de Beer—Lambert s'applique à la raie de résonance 253.7 nm, ce qui, sur le plan théorique n'était pas à priori une certitude [8]. On peut alors calculer un coefficient d'extinction, ϵ, égal à $7.15 \cdot 10^{5}\ \mathrm{m^2\ mol^{-1}}$ en accord satisfaisant avec d'autres valeurs proposées par ailleurs [5, 9—11].

RESULTATS

Les performances d'une telle sonde ont été établies grâce au montage expérimental schématisé sur la Fig. 2. Aucun changement notable dans le comportement de l'ensemble sonde signal n'a pu être observé lors de l'exploration des conditions extrêmes suivantes: débit gazeux, 180 à 1800 $\mathrm{l\ h^{-1}}$; pression: $2 \cdot 10^{-3}$ à 1.3 atm; température: 278 à 343 K.

Le temps de réponse est essentiellement réglé par le temps de passage du mercure entre la sonde et la cellule d'absorption. Avec de courtes canalisations et de forts débits gazeux, il peut être considéré comme instantané.

La durée d'existence d'une telle sonde est très grande et permet de réaliser un nombre de mesures pratiquement infini dans le domaine des faibles concentrations atomiques exploré. Il convient toutefois de se protéger du rayonnement solaire qui provoque une réduction assez rapide de l'oxyde.

Quelques essais ont montré que la sonde présentait une bonne sélectivité vis à vis des atomes d'hydrogène. Aucun signal n'a en effet pu être observé en présence d'azote actif ni en présence des radicaux CH_3 et C_2H_5. Elle s'est par contre avérée très sensible aux atomes de deutérium.

Exemples d'utilisation pratique de cette sonde

La mesure de certaines constantes physicochimiques d'un réactif quelconque peut être effectuée en observant l'évolution de sa concentration dans un réacteur ouvert. De telles expériences ont été menées au laboratoire avec l'hydrogène atomique dont les variations de concentration dans divers types de réacteurs (tubulaires, annulaires, agités, . . .) ont été systématiquement relevées grâce à la sonde à oxyde de mercurique. Mentionnons à titre d'exemple les expériences réalisées avec le montage décrit précédemment (Fig. 2).

Une très faible concentration d'atomes est présente dans de l'hydrogène qui s'écoule en régime laminaire dans un réacteur cylindrique. Les atomes d'hydrogène sont soumis à un entraînement convectif, à des phénomènes diffusionnels et à une réaction de recombinaison sur les parois. On peut montrer [7, 12] que si ce dernier processus est d'ordre un (mécanisme de Rideal) la concentration atomique moyenne dans une section droite du réacteur est une fonction exponentielle décroissante de l'abscisse z.

La Fig. 4 montre que l'expérience confirme ce comportement. Ces résultats ont été obtenus grâce à une sonde en forme de grille ayant un diamètre très proche de celui du réacteur et qu'il était possible de positionner aux abscisses désirées depuis l'extérieur grâce à un système d'aimant.

Une telle forme de sonde possède l'avantage d'intégrer le profil radial de concentration et de fournir ainsi un signal proportionnel à la moyenne de la concentration dans une section droite. On peut montrer, d'autre part, que si

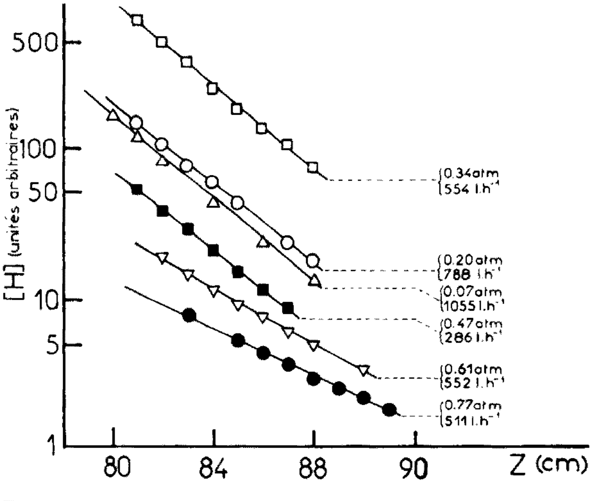

Fig. 4. Représentation graphique des variations de la concentration moyenne en atomes H dans une section droite d'un réacteur tubulaire en fonction de l'abscisse z sous diverses conditions expérimentales.

aucune réaction homogène n'intervient, l'étude de l'évolution de l'argument de cette exponentielle en fonction de la pression permet de déterminer très simplement la diffusivité D et le rendement de recombinaison γ sur les parois. Ces mesures ont été menées systématiquement entre $7 \cdot 10^{-2}$ et 1 atm et 278 et 333 K [13]. L'introduction latérale d'un gaz réactif avec l'hydrogène atomique (comme le monoxyde de carbone, l'éthane ou le propane) a permis également de déterminer un certain nombre de constantes de vitesses homogènes [7, 14].

Il ressort principalement de ces études que les valeurs des divers paramètres physicochimiques ainsi obtenus concordent remarquablement bien avec celles publiées par d'autres auteurs opérant avec les moyens d'analyse habituels (RPE, Lyman α, chimiluminescence, sonde calorimétrique).

Revenons rapidement sur les expériences précédentes pour signaler que si l'on considère que 7 points suffisent à définir une droite, un profil de concentration axial peut être obtenu en un temps proche de 2 min. Cette même opération menée 7 fois sous des pressions différentes permet ainsi d'obtenir les deux paramètres D et γ en 15 min de manipulation effective seulement.

Limites de sensibilité

Celles ci peuvent être évaluées à partir de considérations cinétiques. Lorsque des atomes d'hydrogène circulent dans un réacteur quelconque, ils subissent une recombinaison qui peut s'effectuer

en phase gazeuse: $H + H + H_2 \xrightarrow{k_t} H_2 + H_2$

et sur les parois: $H + \text{paroi} \longrightarrow \frac{1}{2} H_2 + \text{paroi}$

Les études telles que celles qui ont été décrites précédemment ont montré que, dans nos conditions, et en l'absence de gaz étranger, seule une loi d'ordre un a pu être observée, ce qui implique que: $k_p[H] \gg 2k_t[H]^2\,[H_2]$, d'où une condition sur la concentration en atomes $[H] \ll k_p/2k_t[H_2]$, qui, compte tenu des valeurs de k_t [2] et de k_p [7, 13] devient sous 1 atm et pour notre système expérimental: $[H] \ll 5 \cdot 10^{-8}$ mol l^{-1}.

Cette limite repère a pu cependant être atteinte en augmentant volontairement la concentration atomique d'un facteur connu compris entre 10 et 10^2 jusqu'à apparition du processus de recombinaison en phase gazeuse. La limite inférieure de sensibilité a alors pu être estimée à une valeur de [H] voisine de $5 \cdot 10^{-10}$ mol l^{-1}.

En d'autres termes, l'ensemble de mesure que nous avons décrit est susceptible de détecter un taux de dissociation de H_2 voisin de 10^{-8}.

L'ordre de grandeur de ces valeurs a pu être retrouvé [7] en confectionnant une sonde en forme de tube de géométrie très bien définie, par l'utilisation des relations (1) et (4) et des résultats relatifs aux vitesses de réaction sur l'oxyde de mercure(II) obtenus par Elmaleh et coll. [15].

DISCUSSION

Il convient déjà de faire remarquer que le mercure recueilli en aval de la sonde provient non seulement de la réaction des atomes mais également du fait que d'une part HgO manifeste une très légère décomposition dès la température ambiante, et d'autre part que H peut commencer à réagir au dessus de 323 K [4]. Etant donné la validité constatée de la loi de Beer—Lambert, ces phénomènes ne sont cependant pas gênants si l'on règle la ligne de base de l'appareil sur les expériences "à blanc", sans hydrogène atomique.

Si cette limitation supérieure en température n'est pas impérative, il n'en va pas de même aux basses températures où la décroissance importante de la tension de vapeur saturante risque de provoquer la condensation immédiate du mercure. Dans nos conditions, le domaine de température qu'il a été possible de recouvrir est grossièrement compris entre 278 et 343 K. Malgré cette restriction, il est très aisé de passer rapidement d'une température à une autre, ce qui n'est pas toujours le cas avec d'autres techniques (RPE par exemple).

Si, comme nous l'avons signalé, la sonde donne entière satisfaction entre $2 \cdot 10^{-3}$ et 1.3 atm, il faut cependant ne pas oublier que plus la pression est élevée, plus le transfert des réactifs au travers de la couche limite qui entoure l'oxyde est difficile et plus le rendement en mercure est petit.

De par sa nature, la technique présentée ici ne peut être mise en oeuvre que dans des systèmes ouverts. D'autre part, elle doit être réservée aux expériences dans lesquelles les concentrations en atomes sont très faibles. En effet, dans le cas contraire, une accummulation de mercure risque de se manifester au voisinage de la sonde de telle manière que sa vitesse d'apparition en phase gazeuse ne soit plus représentative de la concentration incidente en hydrogène atomique. C'est enfin dans la mesure de variations relatives de concentrations que cette sonde est la plus efficace. Il est cependant possible d'estimer des valeurs absolues grâce à un étalonnage préalable (relation 4), à la connaissance des valeurs de k_1 et k_2 et à l'utilisation des relations (1) ou (3). Il est préférable d'utiliser, à cet effet, le type de sonde en forme de petit tube, d'une part parce que la géométrie est ainsi connue avec plus de précision, et d'autre part à cause du caractère approché du modèle utilisé pour représenter la sonde grille et la mauvaise connaissance des conductances de transfert figurant dans la relation (1).

Ces quelques inconvénients mis à part, cette technique offre d'appréciables avantages.

La très bonne sélectivité de la sonde à oxyde de mercurique a déjà été soulignée: le fait de retrouver certaines constantes relatives aux atomes d'hydrogène déterminées par d'autres auteurs opérant avec des techniques très différentes en est la preuve; d'autre part l'oxyde de mercure(II) semble relativement passif vis à vis d'autres radicaux.

La probabilité pour qu'un choc sur l'oxyde soit suivi de réaction étant relativement faible (de l'ordre de 10^{-3}), une quantité minime d'atomes est donc consommée lors des mesures qui ne perturbent donc pas notablement la cinétique en cours d'étude.

Un autre avantage de la méthode est la possibilité de procéder à un très grand nombre de mesures à la suite sans devoir retirer la sonde du milieu réactionnel pour en renouveler l'oxyde. En outre, la grande souplesse de la méthode optique utilisée ainsi que la rapidité des temps de réponse font qu'il est possible d'observer en temps réel toute évolution dans les concentrations atomiques.

Les limites inférieures de détection sont parfaitement compétitives avec celles d'autres techniques connues mais beaucoup plus sophistiquées et onéreuses. Il convient en effet de souligner la commodité de mise en oeuvre de cette méthode ainsi que son très faible coût.

BIBLIOGRAPHIE

1 B. A. Thrush, Progr. React. Kinet., 3 (1965) 63.
2 W. E. Jones, S. D. Macknight et L. Teng, Chem. Rev., 73 (1973) 407.
3 O. Glemser, U. Hanschild et G. Lutz, Z. Anorg. Chem., 269 (1952) 93.
4 P. Pascal, Nouveau traité de chimie minérale, Masson et Cie, Paris, Tome V, 1962, p. 754.
5 G. Thilliez, Chim. Anal., 50 (1968) 226.
6 B.I.T.C., Anal. Chim. Acta, 72 (1974) 37.
7 J. Lede, Thèse de doctorat Nancy, 1975.
8 J. G. Calvert et J. N. Pitts, Photochemistry, Wiley, 1966, p. 62.
9 J. A. Pinder et D. J. Le Roy, Can. J. Chem., 35 (1957) 588.
10 J. E. McAlduff et D. J. Le Roy, Can. J. Chem., 43 (1965) 2279.
11 L. E. Reid et D. J. Le Roy, Can. J. Chem., 46 (1968) 3275.
12 J. Villermaux, Int. J. Heat Mass Transfer, 14 (1971) 1963.
13 J. Lede et J. Villermaux, J. Chim. Phys., 71 (1974) 85.
14 J. Lede et J. Villermaux, En préparation.
15 S. Elmaleh, D. Chery et J. Villermaux, C.R. Acad. Sci., 272 (1971) 351.

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THE DESIGN AND DEVELOPMENT OF A MULTICHANNEL ATOMIC ABSORPTION SPECTROMETER FOR THE SIMULTANEOUS DETERMINATION OF TRACE METALS IN HAIR

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SUMMARY

A multichannel atomic absorption spectrometer capable of analysing up to nine elements simultaneously in human hair has been designed. Light from an array of hollow-cathode lamps is passed through an electrically heated graphite tube into a direct reading spectrometer. The photomultiplier output is fed into a novel transient signal-processing device which separates the absorption pulse from the continuous background and increases linear range and sensitivity. Solutions containing Ni, Co, Si, Mn, Al, Cu, Ag, Cr and Fe in nanogram and sub-nanogram amounts can be determined with reasonable precision.

Single element a.a.s. with electrothermal pulse vaporization of the sample is well known; the theory and practice have been well documented [1—3]. Multi-element a.a.s. has received less attention; at the present time commercial instruments capable of such analyses are not available.

Butler and Strasheim [4] have described a multi-element spectrometer; by using only half the exit slit of a medium quartz spectrometer and a multi-element hollow-cathode lamp up to four elements were determined simultaneously. Strasheim and Human [5] used a time-resolved spark as the primary light source for multi-element a.a.s. The system had the advantage of easy change of element but suffered from poorer detection limit and lower precision than a conventional a.a. spectrometer. Brech [6] described a system with 45° semi-silvered mirrors to synthesize a single beam. Mavrodineanu and Hughes [7] based a multichannel a.a. spectrometer on two grating spectrometers: one synthesized a composite beam from three separate hollow-cathode lamps, and the other resolved the spectral lines; Mg, Ni and Cr were determined simultaneously by a.a.s. and K, Ca and Na by flame emission spectrometry. This system is suitable for widely spaced spectral lines; closely spaced lines would necessitate more complex synthesizer optics, and the light intensity at the observing spectrometer would be reduced. Pickford and Rossi [8] described a system for the simultaneous

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determination of Co, Cr, Cu, Fe, Mn, Ni and Pb by a.a.s. with an electrothermal atom cell. Background absorption was corrected simultaneously on each channel by seven reference channels and a single multi-element hollow-cathode lamp was used as the source.

Walsh [9, 10] has described several multi-element a.a. spectrometers and has constructed a six-channel a.a. spectrometer with resonance detectors and a multihole burner as the atom cell. This has the advantage that the resonance detectors, effectively acting as monochromators, have very narrow band-passes and their operational wavelength is independent of changes in ambient temperature and pressure. The multihole burner allows different sensitivities to be obtained by adjustment of the path length through the flame. The resonance detector tube, however, suffers from a relatively short lifetime and the whole system is less sensitive than a conventional flame a.a. spectrometer. Walsh has also discussed the use of selective modulation in multi-element a.a. spectrometers.

More recently multi-element spectrometry has been achieved with vidicon tubes. Aldous et al. [11, 12] carried out multi-element analyses with a flame, detecting the radiation with a 500-channel vidicon tube. This system observes a continuous region of the spectrum; the bandwidth, within which the absorption lines of the elements of interest must fall, is dictated by the dispersing power of the grating or prism used. Aldous and co-workers used this system to determine Zn, Cd, Ni, Co, Fe, Mn and Cu in potable waters. Horlick and Codding [13] have described a similar system (bandwidth 13 nm), giving simultaneous determinations of nickel and chromium, and of chromium and iron.

To obtain maximum flexibility of operation in the present work, an attempt has been made to use commercially available hollow-cathode lamps for single elements as much as possible. The instrument, optics, atom cell, electronics and spectrograph described here were designed for the analysis of trace metals in hair [14]. A standard prism spectrograph was employed for spectral dispersion with photomultiplier detection and analog read-out electronics.

INSTRUMENTATION

Optics

A Hilger and Watts medium quartz direct reading spectrometer with transistorized electronics, E 549, was used as the basis of the instrument. A Perkin-Elmer HGA 70 furnace was used as the atom cell; the end cones were drilled out to 9 mm i.d. to increase the aperture. The purge gas was argon at 1500 cm^3 min^{-1}. A simplified block diagram (Fig. 1) shows the main components. Light from the hollow-cathode lamps passes through the furnace on to the vertical 50-μm slit of the spectrometer. The dispersed light falls upon pre-set 35 and 50-μm slits, and then on to photomultiplier tubes. The cathode current passes to the TSP device (see below), and the

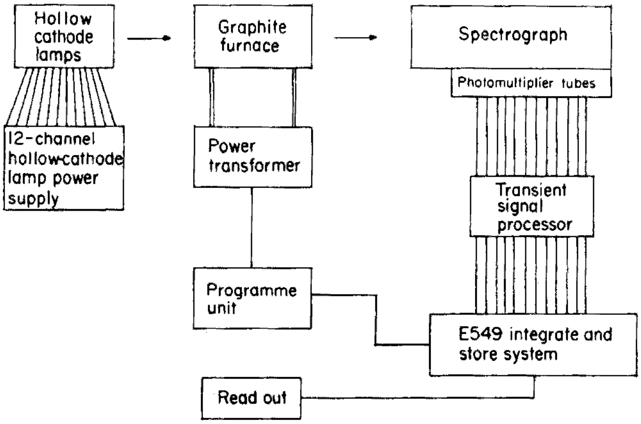


Fig. 1. Block diagram of the system.

signals are fed to the Hilger integration electronics and read out sequentially on a microammeter.

If the total light from the lamps is treated as one object then manipulation by lenses and mirrors will produce an image similar to the object. If the hollow-cathode lamps are in a circular array then the image will be a circular array of images of their cathodes and only the top and bottom images will pass through the vertical slit. The light from each lamp has therefore to be manipulated separately; this was achieved with a small stack of mirrors adjustable individually about horizontal and vertical lines. The original optical system is shown in Fig. 2. To keep light losses to a minimum, wide

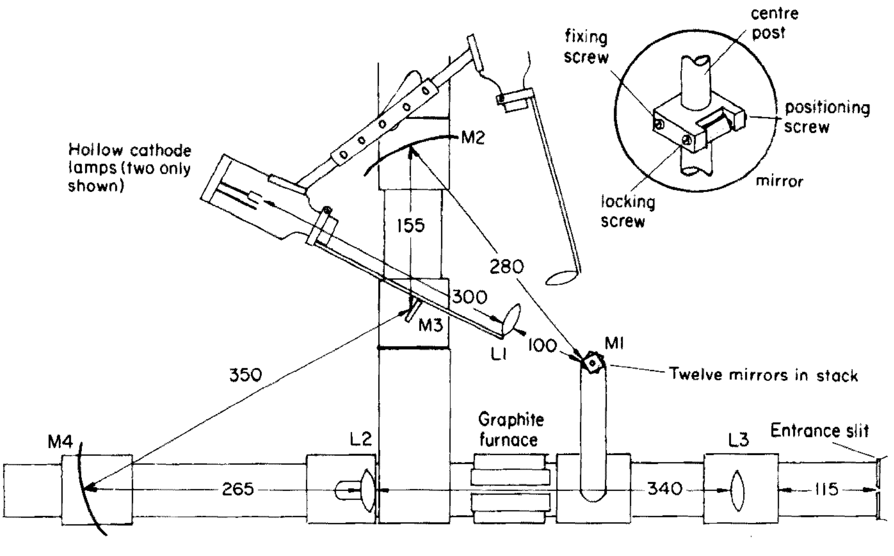


Fig. 2. The original optical system.

aperture optics are required; the spectrometer and graphite furnace are both low aperture (ca. f/12 and ca. f/8, respectively) and thus impose problems. Silica lenses of wide aperture and short focal length are expensive; similar mirrors are relatively cheap. The focal length of mirrors is also independent of wavelength. Mirrors, which allow a more compact system to be devised, were therefore used wherever practicable; a long light path system with wide aperture mirrors was used to keep the light losses to a minimum.

A lens was fixed in front of each hollow-cathode lamp on a rigid arm and an image of the lamp was focused on a mirror in the stack, giving 3-fold diminution of object size. The mirror stack provides an object only 35 mm high with the hollow-cathode images in a vertical alignment. The light from the stack of mirrors (M1 in Fig. 2) is then collected by M2, which reflects and focuses the light on to the plane mirror M3 which reflects it to the large collecting mirror M4. The light is then focused and passed through the furnace on to the spectrometer slit through the quartz lenses L2 and L3. The components used are shown in Table 1.

Electronics

The absorption pulse recorded by the photomultiplier tube (PMT) consists of a short (typically less than 1 s) positive-going pulse on a steady negative d.c. background. It is often necessary to measure very small absorption pulses; this is difficult, largely because of the standing d.c. potential. The electronics of the Hilger and Watts E 549 12-channel direct reading spectrograph, designed for the measurement of continuous emission signals over periods of 5—60 s are not suitable for handling transient absorption signals on high d.c. backgrounds. An electronic device capable of interfacing PMT's with the integrators of the E 549 was therefore designed; the circuit diagram is shown in Fig. 3. The transient signal processor (TSP) consists of an impedance convertor and high impedance load for the PMT, followed by a differentiator, buffer stage, and intergrator, the final output being through a diode; OA1 forms a voltage follower to isolate the high-resistance PMT load resistor from the active differentiator (AD) OA2.

The characteristics of the AD are such that it will differentiate all the frequency components of the absorption peak, below 0.3 of the centre frequency (ωC) of the AD with an error of approximately 2.5 %. This error increases to 50 % at ωC. The frequency response of the AD is shown in Fig. 4.

When the output of the AD (Fig. 5) is integrated by the active integrator (AI) OA4, the original event profile is reproduced with an integrity of 97.5 % but the d.c. and high-frequency components of the original signal are removed by the filtering action of the AD—AI combination. The ωC determined by the values of R_1C_1 and R_fC_f in OA2, is chosen after reference to the event profile and half width to ensure that the integrity is kept as high as practicable; the same value is used for each element to maintain the correct ratios.

TABLE 1

Specifications of the components in the original system

Hollow-cathode lamp supply
12-channel: 2—50 mA, continuously variable at 150—250 V d.c.

Hollow-cathode lamps
Hilger and Watts 'FL 2000' series; Westinghouse High Intensity lamps

Optical components
M1 Twelve 1.5 × 4 mm plane front-surfaced mirrors mounted perpendicularly, permitting movement about the vertical and horizontal axes.
M2 100 mm diam. × 100 mm focal length front-surfaced spherical mirror.
M3 Plane 40 mm diam. front-surfaced mirror.
M4 100 mm diam. × 150 mm focal length front-surfaced spherical mirror.
L1 40 mm diam. × 75 mm focal length, Spectrosil B lens.
$\left.\begin{array}{l}\text{L2}\\ \text{L3}\end{array}\right\}$ 50 mm diam. × 75 mm focal length, Spectrosil B lens

Monochromator
Hilger and Watts Medium Quartz 12 channel direct reading spectrograph
Entrance slit 50 μm × 10 mm; Exit slits 35 μm × 10 mm.
Reciprocal linear dispersion of spectrograph at 20 °C
200 nm: 0.4 nm mm^{-1}
220 nm: 0.6 nm mm^{-1}
280 nm: 1.2 nm mm^{-1}
400 nm: 3.2 nm mm^{-1}

Signal processing
Photomultiplier tubes: EMI 9781 A and B (low noise types)
TSP: Band pass. 0.4—38 Hz 3dB limits. A.c. gain ca. 66 dB

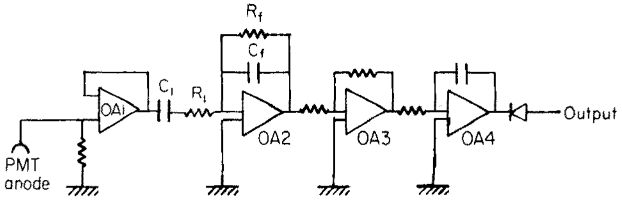
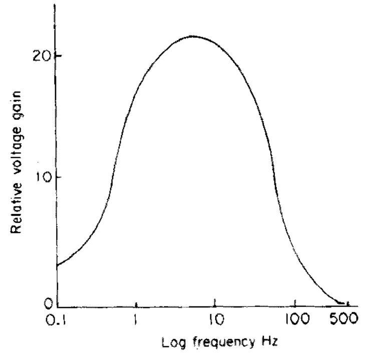


Fig. 3. Circuit diagram for interfacing device.

The re-formed peak, now on a zero volt base level (Fig. 5) is passed to the E 549 electronics via a silicon diode which prevents the discharge of the integrating capacitor back through the charging circuit, so preserving the peak height. The TSP system responded logarithmically to pulse magnitude, probably because of the logarithmic impedance of the series diode seen by the positive integrators. The calibration curves of instrument response vs. concentration of analyte were therefore linear. The curves did not pass through the origin because of the threshold potential of the output silicon diode (0.7 V); smaller pulses cannot pass. Because this diode isolates the



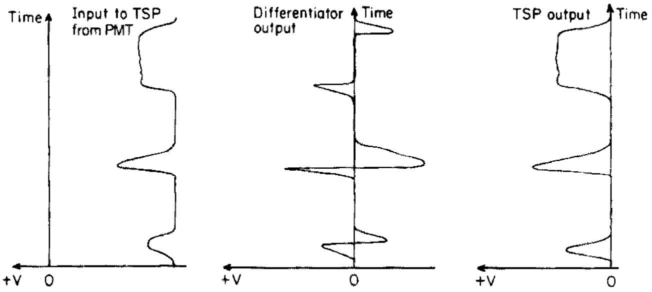


Fig. 4. Frequency response of the active differentiator.

Fig. 5. Conversion of the AD output.

E 549 from pulses of polarity opposite to an absorption pulse, continuum background emission interference is greatly reduced.

The electronics overcome some major problems associated with a.a.s., particularly with simultaneous multi-element a.a.s. The differentiator–integrator system transforms the small pulse on a large d.c. background into a pulse on a zero background. This is simpler to handle and easier to amplify. Two particular problems are overcome: in any system where several sources are combined, increases in background light intensity and the possibility of line overlap become more significant; both phenomena reduce the line: background ratio and hence reduce sensitivity and diminish the working range. By observing only the absorption pulse this reduction can be overcome, but the noise contribution from non-absorbed light is still present (although noise above 40 Hz is reduced). In addition, because of the TSP, the integration cycle of the E 549 only records a signal when an absorption pulse is present, thus maximizing the working range. The continuum background is of less importance since the output circuit is sensitive only to absorption-going pulses. The signals have gone effectively through a logarithmic conversion and are thus linear with respect to concentration.

Atomization difficulties

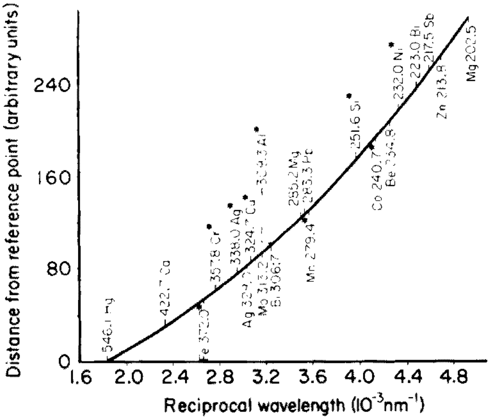
A problem with electrothermal pulse vaporization arises in multi-element a.a.s., since each element has a different rate of evaporation from the carbon furnace; the absorption peaks will be observed at different times of the atomization cycle. This is overcome by integration over 10 s with electronic removal of the d.c. background component.

Line selection for hair analysis

The determination of thirteen elements in hair was studied with a single-channel a.a. spectrometer [14]. Zinc and bismuth gave low results by direct dry ashing of the hair, and the zinc line (307.59 nm) is too close to the aluminium line (309.28 nm) for both to be included in the multichannel instrument; zinc was therefore not included in the multi-element system. The relationship between dispersion and wavelength is important in deciding which lines can be used, and this is shown in Fig. 6. The centre of the slits at the focal plane of the spectrometer cannot be closer than 4 mm apart (the width of the slit mounts). Thus certain lines will be mutually exclusive, e.g. Pb 283.30 nm and Mn 279.48 nm. The final choice of lines is shown in Table 2. The magnesium line at 202.58 nm fell outside the wavelength range of the slit mask.

EVALUATION OF THE SYSTEMS

A block diagram of the initial system is shown in Fig. 1. A trigger line connects the starting circuits of the E 549 unit and the HGA 70 power supply. The time cycles of both electronic systems are adjusted so that the integration cycle (10 s) of the E 549 unit starts at the beginning of the atomization cycle of the HGA 70. While the sample is being ashed in the furnace the E 549 unit is running through its pre-spark cycle (see Table 2). The total cycle time is 95 s. The initial series of calibration curves is shown in Fig. 7; Table 3 gives the concentrations of the solutions used to construct the calibration curves not all of which pass through the origin; this is due to the integrators (Fig. 3) drifting. A calibration curve for chromium could not be obtained at this stage; it was found later that the position of the furnace along the light path was critical. It was also necessary to introduce a diaphragm between furnace and entrance slit, to reduce the amount of continuum radiation reaching the spectrometer. The system was operated with stopped purge gas (argon) during atomization; this causes a certain amount of air to be



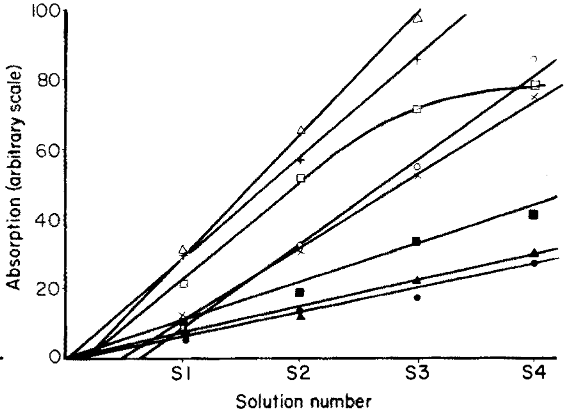


Fig. 6. Relationship between dispersion and wavelength for choice of lines.

Fig. 7. Calibration curves: △ Si, + Mn, □ Ag, ○ Co, × Cu, ■ Al, ▲ Fe, ● Ni. The compositions of S1—S4 are given in Table 3.

TABLE 2

Working conditions
Gas flow (1500 cm^3 min^{-1} argon) vented during atomization.

Programme sequence	HGA 70		E 549	
Dry	100 °C	20 s	Pre-spark	50 s
Ash	750 °C	15 s		
	1100 °C	15 s		
Atomize	2600 °C	15 s	Integrate	10 s
Cool	Cool	30 s		

Element	Wavelength (nm)	Limit of detection (ng)	Linearity max. range (ng)	Range in hair (p.p.m.)[a]
Ni	232.00	0.25	1.5	D.L.—15
Co	240.73	0.05	1	D.L.—3
Si	251.61	0.1	10	2—60
Mn	279.48	0.002	0.2	D.L.—4
Al	309.28	0.05	2	1—50
Cu	324.75	0.01	4	1—60
Ag	338.28	0.005	0.3	D.L.—3
Cr	357.87	0.005	1	D.L.—10
Fe	371.99	0.02	4	5—40

[a] D.L. = minimum determinable amount

TABLE 3

Weight of element (ng) per 10-μl aliquot

Solution	Ni	Co	Si	Mn	Al	Cu	Ag	Cr	Fe
S1	0.3	0.2	2.5	0.05	0.5	1.0	0.1	0.2	1.0
S2	0.6	0.4	5.0	0.1	1.0	2.0	0.2	0.4	2.0
S3	0.9	0.6	7.5	0.15	1.5	3.0	0.3	0.6	3.0
S4	1.2	0.8	10.0	0.2	2.0	4.0	0.4	0.8	4.0

entrained in the furnace. The combination of nitrogen with the hot carbon gives CN band emission; these bands are particularly close to the chromium absorption line at 357.87 nm and may have swamped any small absorption changes given by chromium atoms. Movement of the furnace along the light path caused the radiation from the furnace to be defocused at the slit; thus the amount of CN emission reaching the chromium channel PMT was reduced.

It was thought that the precision (Table 4) could be improved by increasing the light intensity reaching the photomultiplier tubes. Thus two further optical systems with multi-element lamps were tried.

TABLE 4

Relative standard deviations (%) obtained with single element lamps

	Ni	Co	Si	Mn	Al	Cu	Ag	Cr	Fe
S1	36	31	26	21	37	46	19	—	22
S2	37	38	14	23	32	43	23	—	35
S3	26	13	4	11	34	20	11	—	19
S4	32	7	3	11	3	5	8	—	13
EHT setting[a]	9	9	9	9	9	8	7	8	8

[a] The EHT was adjustable from 400—900 V in 10 steps.

Modification to the original optical system

Because of the low light levels involved in the original system, a number of the channels needed very high EHT on the photomultiplier tubes; this introduced noise and in turn led to poor reproducibility at low absorbance. Methods of increasing the light throughout were explored and a simple system with one 7-element hollow-cathode lamp was devised. Of the 7 elements Si, Al, Cu, Fe, Mn, Ca, and Zn, the channels of only the first four of these were aligned on the spectrometer (Table 2). Some light was recorded by the Cr channel; the 7-element lamp was found to emit the Cr spectrum weakly. Si, Al, Cu, Cr and Fe were therefore determined with this lamp. The precision of this system was better than the original, as shown in Table 5. Linear calibration curves through the origin were obtained for the solution concentrations determined (Table 3). Table 5 shows that the EHT levels used were much lower than for the first system (Table 4).

This system was expanded to include the original nine elements. Since 9-element hollow-cathode lamps are not commercially available, a Ni, Co, Mn, Cu, Cr and Fe lamp was used with three single-element lamps. A simplified optical system with the small stack of mirrors was developed (Fig. 8). This retains a certain degree of flexibility; a maximum of five single-element lamps can be used in the vertical array shown and alternative lamps can be quickly fitted. The hole in M4 only slightly reduces the light reflected since

TABLE 5

Relative standard deviations (%) obtained with one multi-element lamp

	Si	Al	Cu	Cr	Fe
S1	15	5	5	—	4
S2	6	5	7	25	6
S3	4	5	6	12	6
S4	8	4	8	13	3
EHT setting	4	0	4	5	1

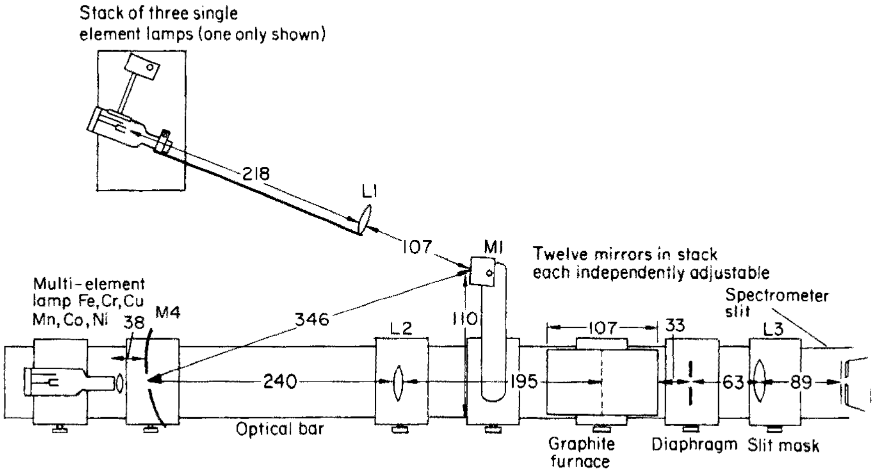


Fig. 8. Final optical system (dimensions in mm).

the image of the lamps fills the whole of M4. The higher light throughput obtained for all channels with this modification is reflected in the lower EHT. settings given in Tables 5 and 6.

The final working conditions and concentration ranges are given in Table 2. The improved precision of the system for 45 replicate analyses is shown in Table 6. This modified optical system was used in the majority of analyses carried out subsequently.

CONCLUSIONS

Some of the difficulties associated with the measurement of the signals from photomultiplier tubes in electrothermal a.a.s. have been overcome by differentiation of the pulses to remove the standing background potential followed by integration to re-constitute the original pulse shape. This signifies signal manipulation and overcomes premature bending of response curves, which would have been caused by high background or line overlap, since only the absorption pulse is measured. The contribution from high background and line overlap serves to degrade the signal:noise ratio and thus decrease the precision and detection limit. An optical system with single-element lamps gave imprecise results which were attributed to low light levels and high EHT settings. Modifications involving the use of multi-element hollow-cathode lamps increased the light throughput and improved the precision.

The authors are indebted to the Central Research Establishment, Home Office, for the loan of equipment and for financial support of J. F. A. and A. J. S.

TABLE 6

45 replicate analyses of S2

	Ni	Co	Si	Mn	Al	Cu	Ag	Cr	Fe	Samples
$\bar{x}$	39	64	55	57	84	69	61	81	34	1—10
s	7	8	4	1	4	2	8	5	1	
s_r (%)	18	12	7	3	4	3	13	6	3	
$\bar{x}$	30	59	50	55	82	70	63	84	32	10—20
s	10	7	3	1	4	5	7	6	1	
s_r (%)	34	13	6	2	5	8	11	8	3	
$\bar{x}$	31	54	49	54	82	66	63	76	29	20—30
s	7	9	4	1	4	2	5	5	1	
s_r (%)	22	17	8	2	5	3	8	6	5	
$\bar{x}$	30	59	52	58	85	67	68	80	31	30—40
s	8	10	4	4	10	7	10	4	2	
s_r (%)	26	17	9	7	12	10	14	5	8	
$\bar{x}$	32	64	48	56	86	68	76	29	29	40—45
s	9	10	3	1	8	1	4	4	1	
s_r	29	16	6	2	9	2	6	6	4	
Mass of analyte (ng)	0.6	0.4	5.0	0.1	1.0	2.0	0.2	0.4	2.0	
EHT setting	7	8	7	2	6	4	6	3	3	

$\bar{x}$ = mean value of absorbances (arbitrary units). s = standard deviation. s_r = relative standard deviation.

REFERENCES

1 G. K. Kirkbright and M. Sargent, Atomic Absorption and Fluorescence Spectroscopy, Academic Press, London (1975).
2 B. L. L'Vov, Atomic Absorption Spectrochemical Analysis, Hilger, London (1970).
3 J. Ramirez-Munoz, Atomic Absorption Spectroscopy, Elsevier, London (1968).
4 L. R. P. Butler and A. Strasheim, Spectrochim. Acta, 21 (1965) 1207.
5 A. Strasheim and H. G. C. Human, Spectrochim. Acta, 23B (1967) 265.
6 F. Brech, Proc. Colloq. Spectrosc. Int., 13th Ottawa, (1967) p. 1191
7 R. Mavrodineanu and R. C. Hughes, Appl. Opt., 7 (1968) 1281.
8 L. C. J. Pickford and G. Rossi, Analyst (London), 98 (1973) 329.
9 A. Walsh, G. F. Kirkbright and R. M. Dagnall, (Eds.), Atomic Absorption Spectrometry, Butterworths, London (1970).
10 A. Walsh, Proc. Colloq. Spectrosc. Int., 13th Ottawa, (1967); p. 257. Pure Appl. Chem., 23 (1970) 1.
11 K. M. Aldous, D. G. Mitchell and K. W. Jackson, Proc. 4th Int. Conf. Atom. Spectrosc., Toronto (1973); Anal. Chem., 47 (1975) 1034.
12 K. W. Jackson, K. M. Aldous and D. G. Mitchell, Spectrosc. Lett., 6 (1973) 315; Anal. Chem., 45 (1973) 1215A; Appl. Spectrosc., 28 (1974) 569.
13 G. Horlick and E. G. Codding, Appl. Spectrosc., 29 (1975) 167.
14 J. F. Alder, A. J. Samuel and T. S. West, Anal. Chim. Acta, submitted.

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THE SINGLE ELEMENT DETERMINATION OF TRACE METALS IN HAIR BY CARBON-FURNACE ATOMIC ABSORPTION SPECTROMETRY

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SUMMARY

Thirteen trace elements in 1-cm samples of hair have been studied. Dry ashing followed by atomization in the carbon furnace and analysis by atomic absorption spectrometry yields reasonably accurate results for Cu, Pb, Al, Fe, Co, Ni, Cr, Si and Mn. Similar analyses for Zn, Bi and Ag in 1-cm samples of hair gave low results compared with wet analyses; these relatively volatile elements may be lost during the ashing procedure. Some information concerning the distribution of these trace elements along the length of individual hairs has also been obtained.

The analysis of hair is important in studies of trace metal metabolism and pollution control, and in forensic work. Until recently trace metals could be determined only in whole hairs, but the advent of electrothermal atomizers in atomic absorption (a.a.s.) has permitted analyses at sub-p.p.m. levels for some elements, in hair samples 1-cm long (100 μg), so that the variation in concentration along the length of a hair can be obtained. A method for the simultaneous multi-element analysis of 1-cm samples of hair has been developed [1] and the results of that work will be described elsewhere [2].

It was considered that the best method of analysis would involve direct introduction of the 1-cm sample of hair into the furnace, followed by ashing to remove organic material which would otherwise cause non-atomic absorption, and atomization. This method was used by Renshaw et al. [3, 4] in a study of lead and copper in human scalp hair.

Dry ashing in the furnace has the advantage of minimizing sample handling with its accompanying problems of contamination and loss. It is not, however, certain that the signal obtained from such a treated sample will represent the true level of an element. The purpose of this work was to evaluate the optimal conditions for such treatment and determine whether valid results were obtained. In all, thirteen elements were examined, viz., Cu, Pb, Zn, Al, Mg, Si, Co, Ni, Cr, Bi, Fe, Mn and Ag. This examination was intended to lead to a procedure for the simultaneous determination of elements in hair,

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and so the conditions finally chosen were necessarily compromises and some elements had to be discarded, even though they were of interest, on the grounds that the pre-treatment of the sample was incompatible with the chemistry of the element or that the element was present in hair in either too low or too high concentration.

EXPERIMENTAL

Washing procedure

The hair samples were washed for 2 h in diethyl ether in a Soxhlet extractor and allowed to dry in clean air. This procedure has been used previously [3—5]; it removes surface grease and dirt but does not eliminate the more firmly bound material; more than 70 % of most elements naturally occurring in hair are retained, and the retention of Cu, Na, Zn, Au, Ca, Sb, Br, Cl and I exceeds 81 % [5].

Equipment

A single-channel system (Hilger and Watts D330 monochromator fitted with a Jobin-Yvon plane grating, 1200 lines/mm, blazed at 330 nm) was used. An EMI 6256B photomultiplier powered by a Brandenberg power supply, Servoscribe strip-chart recorder (response time 250 ms for f.s.d.), and Perkin-Elmer HGA 70 graphite furnace and power supply were used. Hollow-cathode lamps were used in accordance with the manufacturers' instructions. An Oertling QO1 quartz fibre microbalance was used to weigh the samples of hair to 0.1 μg; the reproducibility was better than 0.5 %. An injector consisting of a borosilicate capillary and platinum wire plunger was used to introduce the samples into the furnace. A 10-μl Eppendorf micropipette was used to deliver the solution samples.

RESULTS

Copper

Dry ashing. The samples of hair were washed, weighed and injected into the furnace. The operating conditions are given in Table 1. Atomization of an ashed sample gave an absorption signal of less than 0.3 % on the non-absorbing line at 328.3 nm, and non-atomic absorption was therefore insignificant under these conditions. Analyses were carried out with nitrogen purge gas. There was no loss of copper under these ashing conditions.

Wet ashing. A method of breaking down the organic matrix whilst keeping contamination to a minimum was sought. Hair dissolves rapidly in hot 70 % nitric acid. A weighed section of hair (ca. 1 cm) was inserted into the end of a glass capillary micro-pipette (5 μl volume) which had been previously scribed in the middle. Nitric acid (70 %) was drawn into the pipette to the mark and the pipette was warmed to ca. 60 °C. The nitric acid was moved to and fro to facilitate dissolution of the hair. The dissolved sample was

TABLE 1

Table of working conditions

Element	Wavelength (nm)	Detection Limit in 100 μg of hair (p.p.m.)	Ashing method		Atomization Temperature (°C)
			Time (s)	Programme[a]	
Cu	324.75	0.3	30	7	2500
Pb	283.30	0.1	30	6[b]	2500
Zn	307.59	10	30	6	2300
			10	7	
Al	309.27	0.3	30	7	2600
Mg	202.58	0.1	30	7	2400
Si	251.61	1	30	7	2600
Co	240.73	0.1	30	7	2600
Ni	232.00	0.5	30	7	2600
Cr	357.87	0.1	30	7	2600
Bi	223.06	0.3	30	6	2600
			10	7	
Fe	248.33	0.2	30	7	2400
Mn	279.48	0.03	30	7	2600
Ag	328.07	0.05	30	6	2600
			10	7	

[a] Programme 6 = 750 °C, 7 = 1100 °C

[b] The lead concentration in hair was such that it could be determined with minimum instrumental gain; thus non-atomic absorption was less noticeable and the ashing conditions used kept it at an insignificant level.

injected into the furnace and the pipette was rinsed out. The sample was then dried, ashed, and atomized and the absorption signal measured. The nitric acid blank was 0.01 p.p.m. Cu.

Alternate wet and dry ashing. When analysed by the dry ashing method, hair is heated to 1100 °C (max). prior to atomization to destroy most of the organic matrix; a black residue remains, indicating that complete removal of organic material does not occur. By dissolving the hair samples in nitric acid it was hoped that the organic material would be oxidized and evaporated, leaving only inorganic salts, so that any matrix effects from carbonaceous material would be reduced.

Alternate sections of several hairs were analysed by wet and dry ashing, respectively. The arithmetic means and standard deviations for the copper concentration by the two methods are shown in Table 2 for 40 sections of hair from one head. These results agree with each other and with other published data. The standard deviations are large because they include the error due to the method together with variation along the length.

The matrix effect of nitric acid on the determination of copper was investigated by dissolving some hair in nitric acid and determining copper by standard addition. The slopes of the solution calibration curve, nitric acid standard

TABLE 2

Comparison of pretreatment methods for alternate hair sections

Element	Wet ashing Mixture[a]	Wet ash results p.p.m. ± s.d.	Dry ash results p.p.m. ± s.d.[b]	Literature values for hair (p.p.m.)
Cu	A	12.2 ± 4.2[c]	13.1 ± 2.9	D.L.—500
Pb	A	see text	see text	D.L.—100
Zn	B	[240 ± 10][d] [216 ± 9][d]	60.5 ± 5.5	10—600
Al	C	6.5 ± 0.4[c]	6.3 ± 3.6	1—9
Si	D	12.6 ± 0.6[c]	14.7 ± 2.7	10—28
Co	D	0.31 ± 0.03[c]	0.38 ± 0.10	D.L.—8
Ni	D	2.0 ± 0.3[c]	2.3 ± 0.4	D.L.—28
Cr	D	0.33 ± 0.01[c]	0.33 ± 0.07	D.L.—35
Bi	A	[11.2 ± 0.8][c] [14.4 ± 3.0][c]	1.5 ± 0.5	not reported
Fe	D	18.3 ± 0.9[e]	17.7 ± 2.7	D.L.—250
Mn	A	0.18 ± 0.03[e]	0.15 ± 0.16	D.L.—30
Ag	A	0.3 ± 0.1[e]	0.10 ± 0.02	D.L.—2.6
Mg	A	35.0 ± 5	37.8 ± 10.8	7—240

[a] A. 70 % HNO_3. B. 60 mg of hair dissolved in 1 cm^3 HNO_3—0.5 cm^3 $HClO_4$, made up to 5 cm^3. C. 4 g of hair in 7 cm^3 of 3+1+1 (v/v) HNO_3—H_2SO_4—$HClO_4$ + 1 % MoO_3; with the addition of 70 cm^3 of HNO_3 after dissolution then evaporation to dryness. Make up in 8 % H_2SO_4 to 25 cm^3. D. 700—1000 mg of hair in 3 cm^3 of 25 % (w/v) TMA, made up to 10 cm^3.

[b] The standard deviations include errors in precision etc., but also variation along the length of the hair and over the head which may or may not be random. The hair is so inhomogeneous that it can be justifiably assumed that the precision of the method is much better than the s.d's imply.

[c] By carbon furnace standard addition.

[d] By flame standard addition.

[e] This work was carried out with a multi-element spectrometer [1].

addition and hair digest standard addition agree within 5 %; nitric acid therefore has no appreciable matrix effect on determination of copper. It was concluded that the dry ashing method is accurate for copper. Several hairs were analysed along their length, ca. 1-cm samples being used. The results are shown in Fig. 1.

Lead

Dry ashing. Lead was determined in hair by the dry ashing method already discussed, under the conditions given in Table 1. The atomic line at 283.3 nm is slightly less sensitive than the 217.0-nm line but it is emitted more strongly (× 10) by the hollow-cathode lamp and therefore a better signal: noise ratio is obtained. The lead concentration of several hairs increased from root to tip (Fig. 2); this was also found by Renshaw et al. [3, 4]. Observation of the nearby non-absorbing line at 287.3 nm showed that non-atomic absorption was absent.

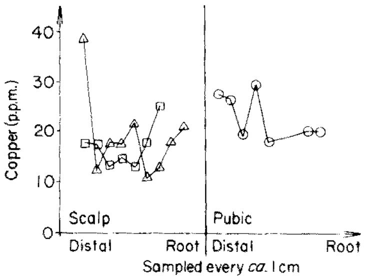
Alternate wet and dry ashing. A procedure similar to that for copper was used; alternate 1-cm sections were analysed by wet and dry ashing. Some typical results are shown in Fig. 3. There is a trend for concentration to increase towards the hair tip. This effectively prohibits any simple statistical analysis. A similar profile of lead concentration along the two hairs from the head of male 2 was obtained by alternate wet and dry ashing (Fig. 3); This is a rather unsatisfactory method of determining the accuracy of the dry ashing method but is the result of the lack of a standard hair and the inherent increase in lead towards the distal end in natural hair. The values found are in agreement with those published [3, 4].

Effect of nitric acid; The effect of nitric acid was found by dissolving several milligrams of hair in concentrated "Aristar" nitric acid and determining the lead by standard addition. A standard addition curve for the pure acid was also obtained. When compared with the lead solution calibration curve, the standard addition curves were found to show a depression.

The alternate wet and dry analysis and standard addition analysis of the acid showed that there is no major difference between wet and dry ashing methods. The results agree with literature values (Table 2) and indicate that the dry ashing technique for lead gives reasonably accurate results. A better comparison cannot be made by this approach because of the variation along the length of the hair.

Zinc

The optimum conditions for determination of zinc in hair are given in Table 1. The 307.6-nm Zn line was used to ensure that the measurements are made on the linear part of the calibration curve. (The 213.9-nm Zn line



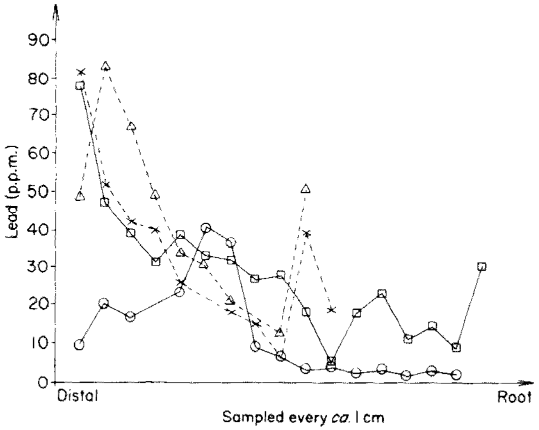


Fig. 1. Copper concentration variation along the length of three male hairs, Male 1.

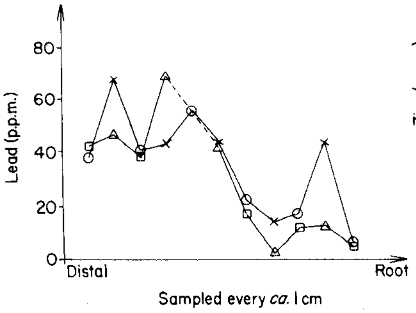
Fig. 2. Lead concentration variation along the length of several hairs. × Male 1 pubic. △ Male 1 scalp. □ Male 2 pubic. ○ Male 2 scalp.

is far too sensitive, because of the high zinc concentration in hair.) The nitrogen purge gas supply was stopped during atomization to give adequate sensitivity (2-fold increase). The minimum ashing conditions necessary to remove all organic matter and prevent non-atomic absorption were: ashing for 30 s at 750 °C followed by 10 s at 1100 °C. Two hairs from a female head were analysed for zinc along their length (Fig. 4); for both hairs the concentration increases towards the distal end. This does not agree with data published by Obrusnik et al. [6] for 10-cm sections of hair, but this analysis sampled the hair every centimetre. The actual values obtained, however, are very low compared with literature values (Table 2), and to check the accuracy of this method a bulk sample of washed hair ends, ca. 3—4 cm long, was analysed by flame a.a.s. and by the above dry ashing procedure (Table 2).

The wet ashing results agree with published data for zinc levels in hair (Table 2). The dry ash results are 3—4 fold lower; this possibly results from loss of zinc on ashing. The boiling point of zinc is 913 °C and the furnace reaches a maximum temperature of 1100 °C. The dry ashing results in Table 2 are given for 33 analyses; since the standard deviation includes the error in the method and any variation in the sample, the method must have a precision of better than 9 %. This is of little use, however, since the accuracy is low.

Other elements

A similar approach was made to the analysis of hair for the other elements studied: Al, Si, Co, Ni, Cr, Bi, Fe, Mn, Ag, and Mg. The results are summarized in Table 2. In order to check the validity of the dry ashing procedure as



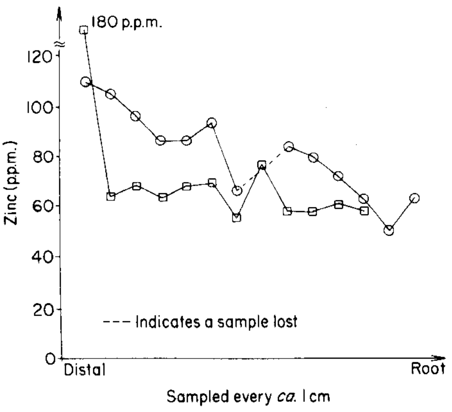
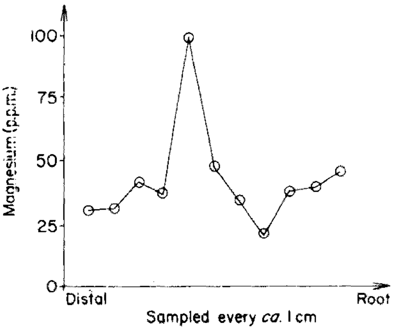


Fig. 3. Alternate wet and dry ashing for lead in scalp hair, Male 2. ○,□ Dry ashing. ×,△ Wet ashing. The dashed line indicates a lost sample.

Fig. 4. Zinc concentration variation along the length of two scalp hairs, Female 1. The dashed line indicates a lost sample.

much as possible, various methods of dissolution were considered. Tetramethylammonium hydroxide (TMA) is a powerful reagent for the dissolution of hair; it was employed for silicon and some other elements. Bismuth, zinc and silver gave low dry ashing results in accord with their volatile nature. The rest of the metals, however, gave reasonably satisfactory agreement between the wet and dry methods. The results for the wet analysis of Ag, Mn and Fe were obtained with a multi-channel a.a. spectrometer [1]. Plots were made of metal concentration vs. position in the hair for a number of elements (Figs. 5—8). For nickel (Fig. 7) there appears to be an increase in concentration towards the root of the hair; a random sample over the head yielded a relative



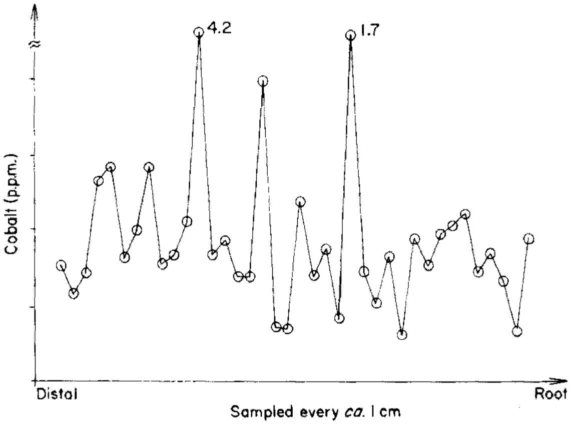
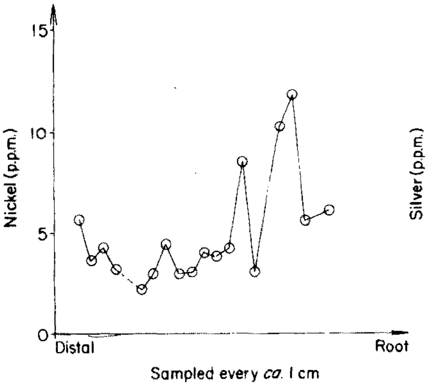


Fig. 5. Magnesium concentration variation along the length of a scalp hair, Male 3.

Fig. 6. Cobalt concentration variation along the length of a scalp hair, Female 2.



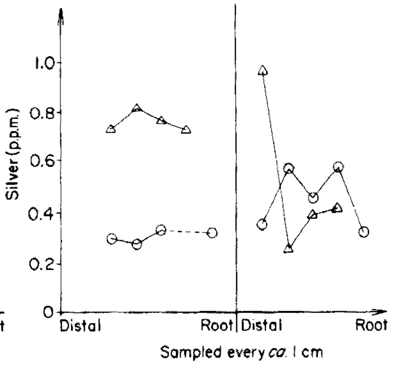


Fig. 7. Nickel concentration variation along the length of a scalp hair, Female 2. The dashed line indicates a lost sample.

Fig. 8. Silver concentration variation along the length of four male scalp hairs, Male 3. The The dashed line indicates a sample lost.

standard deviation of ± 15 % for all the results. The standard deviation of results which are not normally distributed is not very significant but these figures give some idea of the scatter of results likely from one individual; this is important in assessing the method.

CONCLUSIONS

This work illustrates that the dry ashing method is adequate for the analysis of single centimetre segments of hair for most of the metals chosen. A dry method minimizes the handling of the hair and the risk of contamination, and also decreases the analysis time.

For the elements Co, Ni, Cr, Si, Al, Fe, Mn, Mg, Pb and Cu, the dry ashing method gives accurate results. Bi, Zn and Ag determinations give lower results by dry ashing than by wet ashing; the values obtained for zinc are lower than other workers' values. Eminions et al. [7] state that 127 p.p.m. zinc in hair represents the threshold of zinc deficiency, but most of the values obtained by dry ashing in this study were well below this value. Bi, Zn and Ag are fairly volatile elements and may be partially lost during the ashing process. The calibration curves were obtained under similar ashing conditions so these elements may be lost as more volatile organic compounds.

For the more involatile elements the method of dry ashing yields reasonably accurate results, and the method should be extendable to the analysis of other non-volatile elements such as Ba, Be, Ca, Cs, Mo, Ti and V in hair. More volatile elements are liable to be lost during the ashing process necessary to remove the organic matrix.

The data obtained for the variation of magnesium and nickel along the length of hair were not previously available. Data on Ag, Zn and Co were available, but not in such detail; the variation of lead and copper in hair was reported by Renshaw et al. [3]. The variation of magnesium along the length of a hair (Fig. 5) shows a slight increase towards the root although few meaningful observations can be made on the analysis of a single hair. Other analyses showed, however, that magnesium shows a considerable variation within a single individual. The single hair analysed for nickel also shows an increase towards the root (Fig. 7). Obrusnik et al. [6] showed zinc to be relatively constant with a slight decline towards the tip, cobalt to have a steady, nearly five-fold, increase towards the tip, and silver to increase towards the tip but with less uniformity than cobalt. In this study silver was found to show considerable variation from hair to hair (Fig. 8) but less so within an individual hair. One sample (from a different individual) contained no detectable silver; most of the determinations of silver in hair were close to the detection limit; this lowers its usefulness as a diagnostic element since the precision decreases as the detection limit is approached. Zinc increased towards the distal end (Fig. 4), although one hair had a nearly constant concentration. The results for cobalt (Fig. 6) show a nearly constant concentration along the length. The results for copper do not indicate that copper always increases towards the tip, in contrast to the work of Renshaw et al. [3] who did not however present results for many copper analyses.

Both this work and that of Renshaw et al. [3, 4] shows that lead increases towards the distal end. The profile of lead concentration is not identical from hair to hair from the same head and the increase towards the distal parts may not be uniform; in some hairs a dip in concentration near the tip is seen and a sharp change at the root end is also often found. To explain an increase at the tip a mechanism of contamination must be considered; sweat from the apocrine glands at the base of the hair follicle may travel down the hair by capillary action and evaporate, leaving a deposit of trace metals from the sweat, but shampooing would remove such trace metals. Hair can show ion-exchange type properties and it is more likely that the trace metals become firmly bound in the keratin matrix, and are not easily removed by shampooing.

A major difficulty in assessing the validity of this method of analysis of hair is the absence of any reference standard. It was necessary to rely on data obtained by other workers or by sampling from a large bulk of hair, with analysis by two methods. This is hardly ideal, but has proved to be a useful approach to this difficult analytical problem. Because the trace metal concentrations in hair vary so much it is often misleading and unwise to apply simple statistical methods to the results. In general there are erratic changes along the length of a hair and trends often vary from hair to hair. For this reason it is the pattern of the distribution in the hair as much as the actual values of the metal concentration which gives information about the hair. The interpretation of these patterns has, however, yet to be resolved.

The authors are indebted to the Home Office Central Research Establishment for the loan of equipment, for financial support of A.J.S. and J.F.A., and for their help and cooperation. Thanks are due also to Professor R. Belcher of Birmingham University for the loan of the quartz fibre microbalance.

REFERENCES

1 J. F. Alder, D. Alger, A. J. Samuel and T. S. West, Anal. Chim. Acta, 87 (1976) 301.
2 J. F. Alder, A. J. Samuel and T. S. West, Anal. Chim. Acta, to be published.
3 G. D. Renshaw, C. A. Pounds and E. F. Pearson, J. Forensic Sci., 18 (1973) 143.
4 G. D. Renshaw, C. A. Pounds and E. F. Pearson, Nature, 238 (1972) 162.
5 R. F. Coleman, F. H. Cripps and A. Stimson, Atomic Weapons Research Establishment Report No. 0-78/65 (1965).
6 I. Obrusnik, J. Gislason, D. K. McMillan, J. d'Auria and B. D. Pate, J. Forensic Sci., 17 (1972) 426.
7 J. Eminions, J. G. Reinhold, G. A. Kfoury, G. H. Amirhakimi, H. Sharif and M. Ziai, Am. J. Clin. Nutr., 20 (1967) 734.

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RAPID DETERMINATION OF NANOGRAM AMOUNTS OF TELLURIUM IN SILICATE ROCKS

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SUMMARY

A hydride-generation flameless atomic-absorption technique is used to determine as little as 5 ng g^{-1} tellurium in 0.25 g of silicate rock. After acid decomposition of the sample, tellurium hydride is generated with sodium borohydride and the vapor passed directly to a resistance-heated quartz cell mounted in an atomic-absorption spectrophotometer. Analyses of 11 U.S. Geological Survey standard rocks are presented.

Most investigations of hydride-atomic absorption techniques have used only pure solutions. The few applications to real samples [1—3] have involved determinations only in relatively simple matrices, presumably because of the well-known chemical interferences [4—6] with the generation of hydrides. The great simplicity and sensitivity of the technique prompted us to determine its applicability to complex silicate rock matrices.

In a comprehensive study of the geochemistry of tellurium, Sindeeva [7] was limited to reporting most silicate rocks as containing less than 0.1 p.p.m. The absence of more sensitive analytical techniques has meant that only the ore-deposit geochemistry of tellurium is known. Beaty and Manuel [8] described a flameless atomic-absorption procedure with a standard addition technique after chemical concentration to reach lower tellurium abundances in rocks. Watterson and Neuerburg [9] combined chemical separations and concentration of tellurium from 12-g samples with flame atomic absorption to obtain analyses down to 5 ng g^{-1} in rocks. This paper reports a faster procedure for determining as little as 5 ng Te g^{-1} in 0.25-g samples by flameless atomic absorption of the volatile hydride without preliminary chemical separations.

EXPERIMENTAL

Hydride apparatus

The apparatus (Fig. 1) consists of a 25-ml generating flask with a side-arm through which the borohydride solution is injected from an automatic pipet. The generated hydrides are swept in the nitrogen stream (4—4.5 l min^{-1})

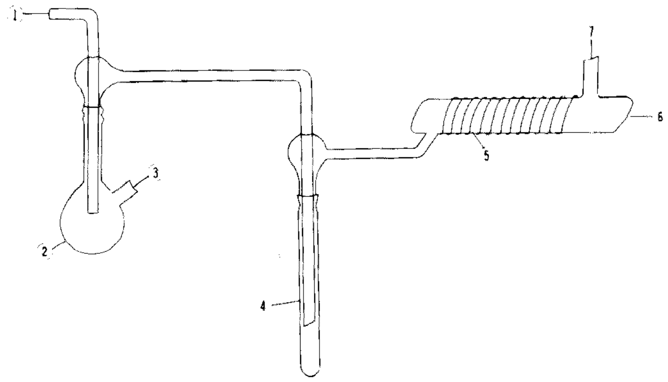

Fig. 1. Hydride apparatus: (1) nitrogen inlet, (2) 25-ml generator flask, (3) side-arm inlet for pipet, (4) 50-ml test tube spray trap, (5) resistance wound quartz cell, (6) light path through quartz windows, (7) gas exit.

through a 50-ml test tube, serving as a spray trap, to a resistance-heated quartz cell mounted in an atomic-absorption spectrometer. The quartz spectrophotometer cell is 2 cm in diameter with a 15-cm light path; it is wrapped with 52 turns of no. 20 kanthal resistance wire. The cell temperature is controlled with a variac adjusted slightly higher than required for the maximum tellurium sensitivity; this temperature, estimated from the color of the cell, is about 1000 °C. The inter-unit connections are made with plastic tubing and are kept as short as possible. Operating conditions of the atomic-absorption spectrometer are those recommended by the manufacturer, and readout is by means of a recorder.

Chemicals

Tellurium standard solution. Dissolve tellurium dioxide in a minimum of nitric and hydrochloric acids and then dilute with 6 M hydrochloric acid to give a stock solution of about 100 μg Te ml^{-1}. Just before use, prepare a 100 ng ml^{-1} solution by dilution of an aliquot of the stock with 6 M hydrochloric acid.

Borohydride solution. Dissolve 5 g of sodium borohydride in 100 ml of water containing two pellets of sodium hydroxide. This solution is stable for several hours at least, but should be prepared just before use.

Procedure

Weigh a 0.25-g sample into a Teflon beaker, add 5 ml of hydrofluoric acid and evaporate the contents to dryness at about 180 °C. Add 15 ml of hydrofluoric acid, 5 ml of nitric acid, and 0.5 ml of perchloric acid to the beaker, and evaporate to dryness at about 120 °C. Add 5 ml of 6 M hydrochloric acid and heat the beaker, covered with a watch glass, at about 80 °C for

30—60 min to dissolve the residue. (Rock solutions prepared this way are quite viscous but essentially clear.) Decant the entire rock solution to the hydride generating flask, and seal the side neck of the flask by insertion of an automatic pipet containing 1 ml of the borohydride solution. When the recorder has returned to a stable baseline, inject the borohydride and measure the peak height of the transient tellurium absorbance signal from the recorder trace.

Then disconnect the generating flask from the system at the ground glass joint, and rinse with water, before adding the next sample.

Standards, prepared by adding 0.01—0.1-ml aliquots of the dilute standard solution to 5 ml of 6 M HCl in the generating flask, are mixed at random through the samples. Sample concentrations are obtained by direct comparison with the peak heights of the standards.

RESULTS AND DISCUSSION

The literature on hydride generation—atomic absorption techniques [1—3, 10—13] is extensive, but there is no consensus of the best conditions. In our hands, many of the published procedures proved less sensitive and precise than expected. Preliminary experiments indicated that the apparent confusion in the literature simply reflects the strong interrelationship among the variables of sample volume and acid concentration, borohydride volume and concentration, nitrogen flow rate, and hydride generator geometry, so that varying these independently can lead to mutually contradictory results.

In view of the need for a routine method for large numbers of samples, conditions were sought where minor variations had little effect on the sensitivity. In particular, the need to heat the samples to effect dissolution in 6 M HCl precluded precise sample volumes, and the unreliability of commercial sodium borohydride precluded exact borohydride concentrations. In the final procedure, sample volumes can vary from 3 to 7 ml, and borohydride concentration can vary from 2 % to 8 % without important effect on the sensitivity. In 2 months experience with this method in routine use, the slope and intercept of the standard curve remained constant from day to day, confirming that the generating conditions were not critical. These conditions do not give the maximum sensitivity; the sensitivity can be increased, by at least a factor of 2, by eliminating the test tube spray trap and altering the nitrogen flow and borohydride concentration. Unfortunately, the higher sensitivity can be maintained only by constant attention to details and frequent cleaning of the cell. Sensitivity is also dependent then on bulk sample composition.

Early experiments proved that injecting the hydride gas directly into the atomic-absorption flame could not give adequate sensitivity for the low levels of tellurium expected in rocks. Decomposition of the hydride in a flame-heated quartz cell as described by Thompson and Thomerson [11] gave adequate sensitivity, but the short lifetime of the cell, because of the high-temperature devitrification of the quartz, argued against use of this system for routine analyses. Chu et al. [13] were unable to operate their resistance-heated cell at high temperatures because of an increasingly high blank response in their attempted determination of arsenic. No difficulties were found in operating the present cell at temperatures somewhat greater than are required for maximum sensitivity in determinations of tellurium, selenium, bismuth, and antimony. However, it was often necessary to condition the system upon first heating by running two or three blanks, after which the tellurium blank should be zero. With the procedural conditions and the cell maintained near 1000 °C, the sensitivity is about 1 ng of tellurium (0.2 ng ml^{-1}) for 1 % absorption; this allows the determination of as little as 5 ng g^{-1} tellurium in rocks.

Interferences with hydride generation, particularly by the acid-sulfide elements, are well known [4—6]. Contradictions within the literature and experience in this work suggest that the severity of the interference is highly dependent on the precise conditions used for hydride generation. The present system was tested for the effects of iron and copper, the most serious interferences expected in rocks. Up to 100 mg of iron, as iron(III) chloride, had no effect on the generation of tellurium hydride. The effect of copper, as copper(II) chloride, was an increasing suppression of tellurium hydride at levels exceeding about 50 μg of copper; 100 μg of copper caused 40 % suppression of the signal whereas 1000 μg caused 90 % suppression. Thus the applicability of the procedure is limited to rocks containing less than 200—300 μg Cu g^{-1}. Fortunately, most ordinary rocks contain less copper than this, whereas mineralized samples containing abundant copper are also relatively rich in tellurium, allowing much smaller samples to be taken. Attempts to eliminate the interference of copper by additions of potassium iodide were completely successful; however, in the presence of iodide, iron (presumably iron(II)) completely suppressed the formation of tellurium hydride, and thus this solution is not possible for rocks.

TABLE 1

Tellurium by standard addition

Rock	Tellurium ng g^{-1}	
	Standard addition[a]	Direct comparison with standards[b]
BHVO-1, basalt	4.9 ± 1.5	6.3 ± 0.7
GSP-1, granodiorite	18 ± 2	19 ± 2.9
SDC-1, schist	6.8 ± 4.2	5.5 ± 2.7
BCR-1, basalt	1.1 ± 1.2	0.0 ± 0.4

[a] Least-squares line fitted to 16 points: 4 replicates of 0, 2, 5, and 10 ng of added tellurium. Error is the calculated error of intercept.

[b] From analysis of variance, Table 2.

TABLE 2

One-way analysis of variance

Rock	Tellurium, ng g^{-1}				
	Bottle[a]				Mean[b]
	A	B	C	D	
BHVO-1	5.3	6.8	6.1	6.1	6.3 ± 0.7
	5.3	6.8	4.6	6.8	
	6.1	7.6	6.1	6.1	
	7.6	7.6	6.1	6.1	
SDC-1	4.6	11	3.9	4.6	5.5 ± 2.7
	5.3	7.6	5.3	4.6	
	2.4	3.1	12	6.8	
	2.4	4.6	4.6	5.3	
BCR-1	0	0	0	0	0.0 ± 0.4
	0	0	2.4	0	
	0	0	0	0	
	0	0	0	0	
GSP-1	19	22	19	16	19 ± 2.9
	23	22	16	24	
	17	16	21	19	
	18	22	16	20	

[a] F-test shows no significant difference among bottles at 95 % confidence level.
[b] Analytical error calculated from "within bottle" variance.

To make more realistic tests for interferences in rocks and to confirm that tellurium was not lost during the decomposition process, four rocks of widely different composition were selected for a standard addition experiment. Sixteen 0.25-g samples of each rock were divided into four sets of four replicates and the replicates were spiked with 0, 2, 5, and 10 ng of tellurium. After the usual decomposition and analysis, the data were fitted with a least-squares line, and the concentration of tellurium in the rock determined from the intercept. These data are in good agreement with analyses obtained by direct comparison with pure standard solutions (Table 1), which indicates both an absence of interferences and no loss of tellurium in the decomposition.

The analytical precision was estimated from an analysis of variance experiment which also provided a test of the homogeneity of the rocks [14]. Four bottles of each of four U.S.G.S. standard rocks were analyzed in quadruplicate. These data are given in Table 2 with the mean and analytical precision calculated from the analysis of variance. The analysis of variance also showed no significant (95 %) differences in the tellurium content among bottles of any specific rock, and thus these samples may be accepted as homogeneous within the limits of the analytical method.

TABLE 3

Tellurium in U.S.G.S. standard rocks

Rock	Te (ng g^{-1})	Rock	Te (ng g^{-1})
Granite, G-1	7, <5, <5	Rhyolite, RGM-1	<5, <5, <5
Diabase, W-1	<5, <5, <5	Basalt, BHVO-1	6[a]
Andesite, AGV-1	<5, <5, <5	Mica schist, SDC-1	6[a]
Granite, G-2	<5, <5, <5	Granodiorite, GSP-1	19[a]
Quartz latite, QLO-1	<5, <5, <5	Basalt, BCR-1	<5[a]
Nepheline syenite, STM-1	<5, <5, <5		

[a] Mean of 16 analyses from Table 2.

A further check of the analytical precision was made by decomposing eight samples of the SDC-1 rock, combining the individual solutions, and analyzing six aliquots. This procedure eliminated sampling and decomposition errors, leaving only the error associated with generation and measurement of the hydride. Comparison of this result (7.8 ± 1.4 ng Te g^{-1}) with the result in Table 2 shows that the total error is about equally distributed between preparation and measurement of the rock solution.

Analyses of some of the U.S.G.S. standard rocks are reported in Table 3. A comparison with previous values is possible only for GSP-1 and BCR-1. The present value of 19 ng Te g^{-1} in GSP-1 agrees well with other atomic-absorption determinations [8, 9] of 20 and 21 ng g^{-1}. A neutron-activation technique [15] has given 5.5 ± 2.2 ng Te g^{-1} in BCR-1, which is not incompatible with the present upper limit.

The analytical method described here is very rapid, quite sensitive, and reasonably accurate and precise. Although neither the sensitivity nor the precision may be adequate for detailed geochemical research, this method should be well suited to broad reconnaissance studies of the natural occurrence of tellurium.

REFERENCES

1 K. T. Kan, Anal. Lett., 6 (1973) 603.
2 F. J. Schmidt and J. L. Royer, Anal. Lett., 6 (1973) 17.
3 J. A. Fiorino, J. W. Jones and S. G. Capar, Anal. Chem., 48 (1976) 120.
4 E. B. Sandell, Colorimetric Determination of Traces of Metals, Interscience, New York, 1959.
5 A. E. Smith, Analyst, (London), 100 (1975) 300.
6. F. D. Pierce and H. R. Brown, Anal. Chem., 48 (1976) 693.
7 N. D. Sindeeva, Mineralogy and Types of Deposits of Selenium and Tellurium, Interscience, New York, 1964.
8 R. D. Beaty and O. K. Manuel, Chem. Geol., 12 (1973) 155.
9 J. R. Watterson and G. J. Neuerburg, J. Res. U.S. Geol. Surv., 3 (1975) 191.
10 F. J. Fernandez, At. Absorpt. Newslett., 12 (1973) 93.
11 K. C. Thompson and D. R. Thomerson, Analyst (London), 99 (1974) 595.
12 K. C. Thompson, Analyst (London), 100 (1975) 307.
13 R. C. Chu, G. P. Barron and A. W. Baumgarner, Anal. Chem., 44 (1972) 1476.
14 F. J. Flanagan, U. S.Geol. Surv. Prof. Paper, 840 (1976) in press.
15 R. R. Keays, R. Ganapathy, J. C. Laul, U. Krähenbühl and J. W. Morgan, Anal. Chim. Acta, 72 (1974) 1.

Analytica Chimica Acta, 87 (1976) 329—339

ÉTUDE SPECTROMETRIQUE D'UN PLASMA INDUIT PAR HAUTE FRÉQUENCE
II. DIFFÉRENTS TYPES D'EFFETS INTERÉLÉMENTS OBSERVÉS

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(Reçu le 9 janvier 1976)

RÉSUMÉ

Une étude de la nature de certaines interférences a été réalisée dans un plasma induit par haute fréquence utilisé comme source d'excitation en spectroscopie d'émission. Elles ont été classées en interférences chimiques, de nébulisation, d'atomisation et spectrales. Les interférences chimiques sont négligeables sinon inexistantes et celles de nébulisation peuvent être levées aisément. Les interférences spectrales ont été résolues à l'aide d'un dispositif de correction spectrale. La seule interférence résiduelle provient de l'atomisation. Elle demeure faible mais mérite une étude particulière.

SUMMARY

A study of different types of interferences has been carried out with an inductively coupled plasma source for emission spectrometry. The interferences are classified as chemical, nebulization, atomization and spectral. Chemical interferences are negligible and nebulization ones can be avoided easily. Spectral interferences can be resolved with the use of an electronic correction device. The only residual interferences are due to atomization; although these are low, they can be avoided only by precise information on the physicochemical mechanisms involved.

Les très bons résultats analytiques fournis par le plasma induit par haute fréquence utilisé comme source spectroscopique à partir de solutions contenant l'espèce à analyser justifient que l'on étudie de manière plus systématique les différents effets interéléments (interférences) susceptibles de perturber des dosages. Les différents auteurs [1—7] s'accordent à dire qu'en général les interférences sont réduites considérablement par rapport aux flammes chimiques classiques. Néanmoins certaines interférences résiduelles n'ont pu encore être éliminées ni même expliquées. C'est pourquoi nous avons repris cette étude à l'aide d'un nouveau générateur de plasma induit par haute fréquence afin d'essayer de déterminer l'origine de ces interférences.

PARTIE EXPÉRIMENTALE

Appareillage

Il est identique à celui décrit dans la partie I [8]. Pour cette étude, le générateur haute fréquence fonctionne avec une puissance appliquée de 1,3 kW. La seule modification apportée est dans le système de désolvatation de l'élément. Nous avons utilisé soit un four chauffant à 500 °C sur une courte distance (14 cm) soit un four chauffant entre 140—220 °C sur une plus longue distance (70 cm).

Les débits adoptés sont 12 l min^{-1} pour le gaz plasmagène et 0,75—1,15 l min^{-1} pour le gaz transporteur d'aérosol, la tête d'injection du plasma étant placée verticalement.

Préparation des solutions aqueuses

Les différents éléments ont été dissous dans l'eau généralement neutre à partir de NaCl, $Al(NO_3)_3.9\ H_2O$, H_3PO_4, $CaCl_2$, $Cr(NO_3)_3.9\ H_2O$, CdO (en milieu chlorhydrique). Pour l'étude des éléments comme le vanadium, le titane, le lanthane le tungstène ou le cérium dans les matrices, la dissolution se fait en milieu acide à partir de V_2O_5 et $Ce(SO_4)_2 \cdot 4\ H_2O$ (milieu sulfurique), Ti métal (dissous en milieu nitrique), $La(NO_3)_3 \cdot 6\ H_2O$, et WO_2Cl_2 (milieu fluoronitrique).

INTERFÉRENCES CHIMIQUES

Il est bien connu que ce type d'interférences, dû à la stabilité des complexes chimiques formés, est rendu négligeable du fait de la température élevée généralement fournie par les plasmas haute fréquence. Comme dans le cas de notre appareillage, la température mesurée sur les éléments excités est inférieure à 5000 K [9], nous avons voulu vérifier si elle était encore suffisante pour supprimer les interférences chimiques. Pour cela nous avons étudié deux types d'interférences bien connues: le système Ca—PO_4 et le système Al—Ca. Fassel et coll. [3] ont décrit les causes de ces interférences dues à la formation de composés réfractaires. Pour cette étude de l'influence de l'ion PO_4^{3-} et de l'ion Al^{3+} sur le calcium neutre et ionisé, nous avons choisi les raies Ca I 422,7 nm et Ca II 393,3 nm.

Sur la Fig. 1, nous avons porté les résultats obtenus pour une concentration en Ca^{2+} de 20 $\mu g\ ml^{-1}$, les intensités étant exprimées par rapport à l'intensité obtenue en l'absence d'ion interférant. L'influence consiste en un léger accroissement pour un rapport élevé de l'ion interférant sur l'ion Ca. Ceci montre que les combinaisons chimiques bien connues de calcium avec les phosphates et aluminates sont détruites malgré la température relativement basse du plasma. Cela s'explique par le temps de séjour élevé des particules à analyser dans la zone d'excitation, le nombre de spires de l'inducteur étant important (cinq). Le phénomène observé est d'une autre nature: nous verrons plus loin que ces variations sont dues essentiellement à l'atomisation.

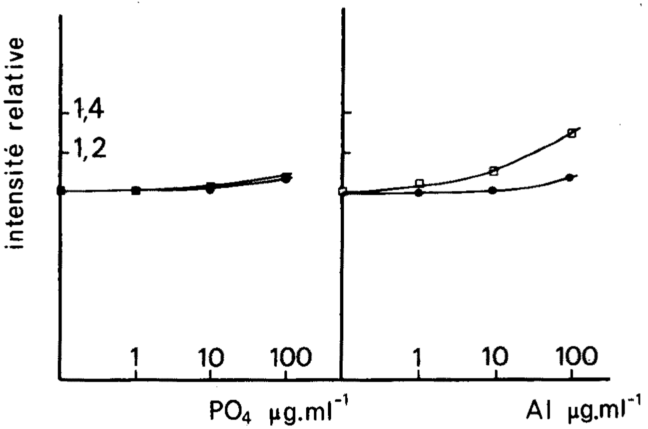

Fig. 1. Interférence des ions phosphate et aluminium sur les raies du calcium I et II.
□ Ca I 422,67 nm. ● Ca II 393,37 nm.

Interférences dues à l'anion

Nous avons étudié l'influence de plusieurs anions sur l'intensité d'une raie d'analyse d'un même cation. Notre choix s'est porté sur le sodium (la désolvation est utilisée dans tous les cas). Pour les anions sélectionnés (Cl^-, NO_3^-, HPO_4^{2-}, $P_2O_7^{4-}$, SO_4^{2-}, $S_2O_8^{2-}$, $S_2O_3^{2-}$), l'influence sur l'intensité de la raie Na I 330,2 nm peut être considérée comme négligeable (variations par rapport à Cl^-: 97—101 %).

Interférences dues à la composition de la matrice

Nous avons étudié l'influence de la composition de la matrice sur l'émission de raies I et II d'un élément. Nous avons choisi comme élément test le vanadium en utilisant les raies V I 437,9 et V II 292,4 nm, raies les plus sensibles dans chacun des deux états d'ionisation. Les différentes matrices utilisées sont indiquées sur le Tableau 1, la variation de signal obtenue étant repérée par rapport aux signaux de vanadium seul. On peut observer que cette influence est faible sinon négligeable, à l'exception de sodium, ou on observe un phénomène semblable à celui que l'on retrouvera plus loin sur le calcium, mais avec un ordre de grandeur encore plus important.

INTERFÉRENCES SPECTRALES DUES À LA MATRICE FER

L'aptitude du plasma à analyser un grand nombre d'éléments dans une gamme de concentration étendue, est intéressante dans le cas de l'analyse des aciers [5]. Nous avons cherché dans un premier stade à étudier la perturbation apportée par la présence du fer non seulement en tant que matrice mais aussi en tant qu'interférant spectral, car cet élément possède un spectre très riche en raies I et II dans le plasma. Notre choix s'est porté sur le tungstène, le cérium, le titane et le lanthane, dont les limites de detection en solution pure

TABLEAU 1

Influence sur les raies I et II du vanadium (1 μg ml^{-1}) de la composition d'une matrice

Composition de la matrice (100 μg ml^{-1})	Intensité raie I 437,9	Intensité raie II 292,4
pas de matrice	100	100
Zn	97	100
Fe	95	103
Al	97	99
Cu	103	101
Na	225	200

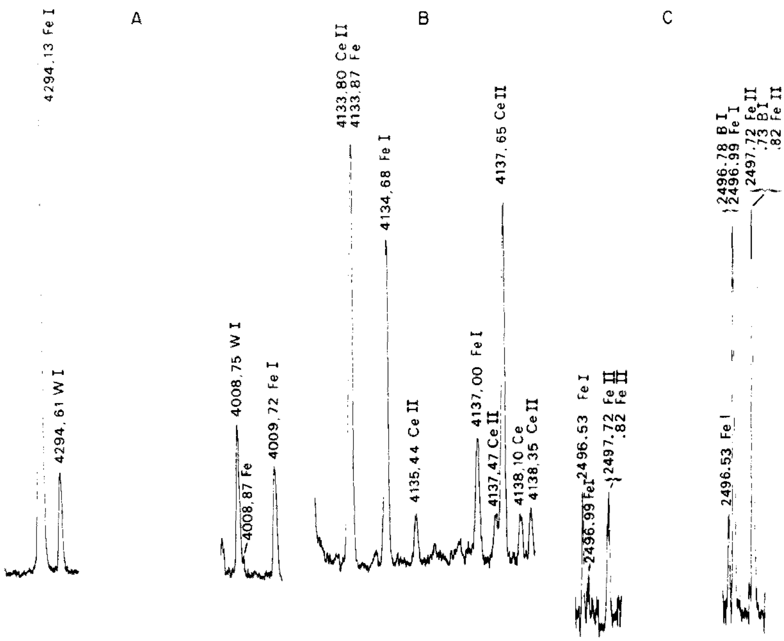

Fig. 2. Interférence spectrale du fer sur (A) le tungstène (W 0,5 %); (B) le cerium (Ce 0,5 %); (C) le bore (B 5 %).

sont de l'ordre du ng ml^{-1}.

Nous avons tout d'abord examiné si, sur les raies les plus sensibles utilisées pour l'étude des limites de détection [8], la présence d'une raie du fer pouvait interférer. Sur la Fig. 2(A), nous donnons un exemple pour le tungstène. A la raie W I 400,875 utilisée habituellement se superpose en partie la raie Fe 400,887 ce qui nous a obligés à travailler avec la raie W I 429, 46. De même sur la Fig. 2(B), nous avons représenté l'interférence due à la raie 413,387 du fer sur la raie II 413,380 du cérium. Nous avons pris la raie voisine II 413,765 qui n'est pas perturbée par une raie du fer et reste d'intensité comparable. Pour le lanthane, notre choix s'est porté sur la raie La II 408,67, la raie La II 394,910 étant superposée à la raie Fe 394,915. Seul le titane avec la raie Ti II 334,94 ne nous a pas posé de problème. Pour ces longueurs d'onde, nous avons utilisé la ref. [10].

Notons que ces interférences ne sont gênantes que lorsque les raies sont séparées par moins de 0,02 nm. Cet écart minimum est lié à l'élargissement des raies dans le plasma et non aux performances du dispositif dispersif. La bande passante du monochromateur utilisé avec des fentes d'entrée et sortie de 30 μm est de 0,005 nm à 400 nm.

Sur le Tableau 2, nous avons porté les limites de détection obtenues avec et sans fer, le fer étant à la concentration de 1 g l^{-1}. On constate que la présence de fer ne change pas sensiblement la valeur de ces limites de détection et que les légers reculs observés proviennent essentiellement des changements de raies destinés à éviter l'interférence spectrale du fer. Dans le cas du titane, il n'y a aucune variation. Aussi, la limite de détection de l'élément rapportée à la quantité de fer est déterminée par la concentration maximale de fer qu'il est possible d'introduire dans le plasma.

Le cas du bore est plus délicat. En effet, comme le montre la Fig. 2(C) des raies du fer viennent se superposer aux raies d'analyse du bore. Ces raies, particulièrement la raie Fe I 249,699, sont peu intenses mais suffisantes pour gêner considérablement le dosage du bore: en effet, la concentration en fer étant maintenue constante, la limite de détection est seulement de 1000 p.p.m de bore par rapport au fer. Le spectre du bore étant pauvre en raies, il n'est pas possible de trouver une autre raie d'analyse qui soit distante d'au moins 0,02 nm d'une raie de fer. Pour lever cette interférence, nous avons dû avoir recours au traitement du signal par la méthode de correction spectrale. Le principe de cette méthode consiste à mesurer simultanément l'intensité d'émission B + Fe à la longueur d'onde 249,772 + 249,773 + 249,782 et l'intensité d'émission du fer seul sur la radiation Fe II 251,176 nm. Un microcalculateur analogique traite les signaux et donne le signal corrigé du bore seul (Fig. 3). Les gains des amplificateurs sont réglés de telle façon que $G_1 = G_3.\ K_3/K_1$; $G_2 = G_3.\ K_3/K_2$; et $G_4 = G_5.\ I(\mathrm{Fe})_r/I(\mathrm{Fe})_i$.

Il nous a été possible de retrouver la même limite de détection pour le bore dans une solution contenant 100 p.p.m. de fer, qu'en solution pure, soit 2 p.p.b. L'efficacité dans l'application de cette méthode dépend du respect — dans la mesure du possible — des critères de choix de la raie de compensation tels

TABLEAU 2

Limites de détection (en ng ml^{-1}) obtenues avec et sans fer (1 g l^{-1})

Élément	λ	Limite sans fer	λ	Limite avec fer
W	I 400,87	2	I 429,46	15
Ce	II 413,38	2	II 413,76	5
Ti	II 334,94	0,25	II 334,94	0,25
La	II 394,91	0,15	II 408,67	0,30

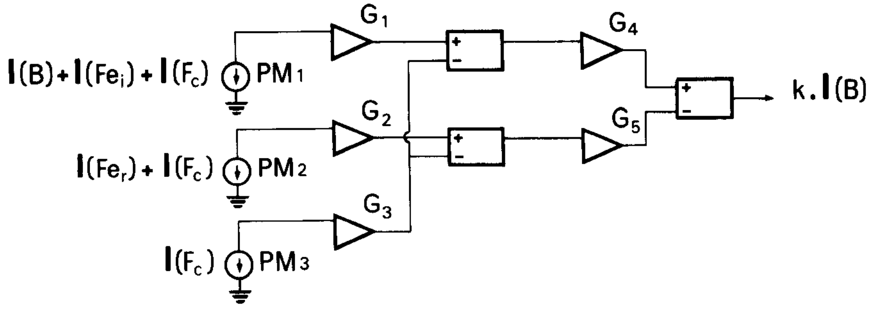

Fig. 3. Schéma de principe de l'appareil utilisé pour la correction spectrale. K_1, K_2, K_3 gains des photomultiplicateurs (PM) 1, 2, 3. I (Fe_i) raie interférante du fer. I (Fe_r) raie de référence du fer. I (B) raie d'analyse du bore. I (Fc) fond continu. G gain des amplificateurs opérationnels, G_1, G_2, G_4: variables, G_3, G_5: fixes.

qu'ils ont été décrits précédemment [8] pour la méthode d'absorption atomique à deux longueurs d'onde.

Dans le cas d'éléments à analyser dans une matrice fer, tels que le tungstène ou le cérium, cette méthode devrait permettre par retour aux raies d'analyse les plus sensibles, de retrouver les mêmes limites de détection que sur les solutions pures.

ÉTUDE D'AUTRES EFFETS INTERÉLÉMENTS

Choix des interférences

Nous avons déjà montré [2] que l'influence d'un élément de faible énergie d'ionisation ne pouvait s'expliquer pas la variation de la densité électronique résultant de l'addition d'une certaine quantité de cet élément. Afin de vérifier cela avec une nouvelle source de conception différente, nous avons repris l'étude de l'influence du sodium sur le phosphore et le chrome. Nous avons également étudié l'influence du sodium sur le cadmium et le calcium pour les comparer à d'autres résultats précédement publiés [3]. Ces éléments représentent une gamme d'énergie d'ionisation allant de 6,11 eV à 11,0 eV.

Nous avons fait varier la concentration de sodium jusqu'à 1 g ml^{-1} pour des concentrations des éléments respectivement de 50 $\mu g\ ml^{-1}$ pour le phosphore, de 26 $\mu g\ ml^{-1}$ pour le chrome, de 56 $\mu g\ ml^{-1}$ pour le cadmium, et de 20 $\mu g\ ml^{-1}$ pour le calcium. Nous avons suivi les variations d'intensité à l'aide des raies P I 253,5; Cr I 425,4 et Cr II 284,3; Cd I 228,8 et Cd II 226,5; et Ca I 422,7 et Ca II 393,3; et cela pour trois débits d'injection de l'aérosol et pour trois hauteurs d'observation repérées par rapport à la partie supérieure de l'inducteur. L'observation se fait à travers le tube de silice. Nous avons représenté les résultats obtenus sur le Fig. 4(A—D).

Nous voyons que la variation la plus importante est celle due à l'influence du sodium sur la raie du phosphore (Fig. 4A), phénomène que nous avions déjà trouvé avec un plasma travaillant à 5 MHz. Par contre, les variations

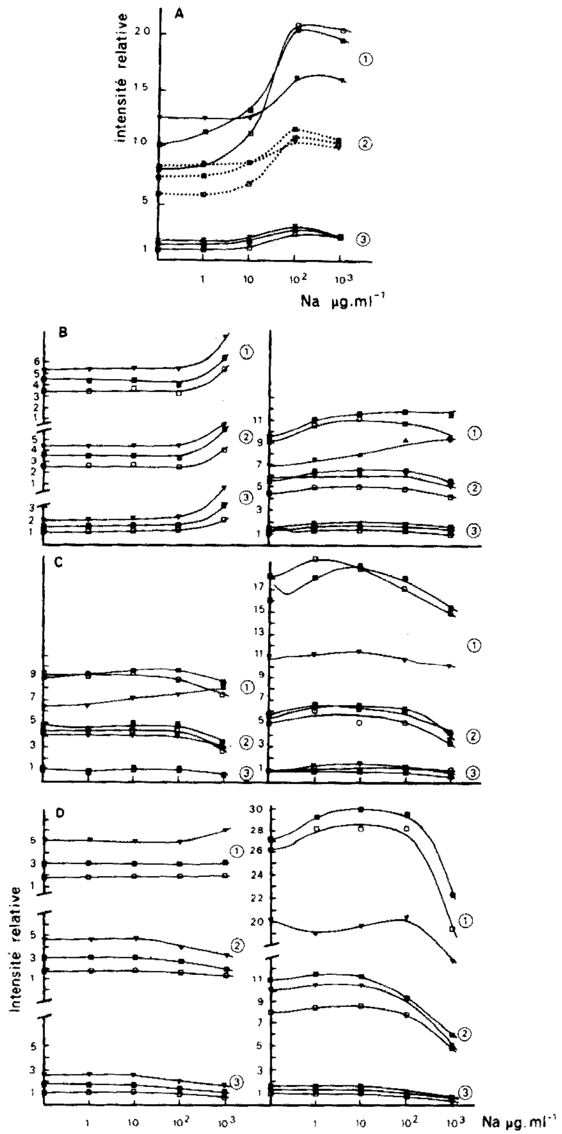

Fig. 4. Variation des intensités de raies par rapport à l'intensité mesurée pour une hauteur d'observation h = 25 mm et un débit d'injection de l'aérosol de 0,75 l min^{-1}, en fonction de la concentration en sodium. □ 0,75, ■ 0,95, △ 1,15 l min^{-1}, ① h = 5, ② h = 15, ③ h = 25 mm. (A) Variation du signal de la raie 253,5 P I (50 µg P ml^{-1}). (B) Variation du signal des raies 422,7 Ca I (gauche) et 393,3 Ca II (droite) (20 µg Ca ml^{-1}). (C) Variation du signal des raies 228,8 Cd I (gauche) et 226,5 Cd II (droite) (56 µg Cd ml^{-1}). (D) Variation du signal des raies 425,4 Cr I (gauche) et 284,3 Cr II (droite) (26 µg Cr ml^{-1}).

obtenues sur la raie I du chrome peuvent être considérées comme faibles, celles sur la raie II du chrome consistant en un affaiblissement du signal aux fortes concentrations du sodium (Fig. 4D). Il faut remarquer sur ces figures que le paramètre débit d'aérosol n'a pas une grande influence: il entraîne uniquement un décalage de la courbe en intensité, sa forme étant conservée. Il est en de même pour la hauteur d'observation quoique ces effets soient d'autant moins marqués que l'on s'éloigne de l'inducteur.

Etude de l'influence du sodium sur l'intensité du calcium

Nous avons ensuite comparé les résultats obtenus sur le calcium ainsi que sur le cadmium I et II à ceux de Fassel et coll. [3]. Dans le cas du calcium I, ces auteurs observent un accroissement en fonction de la concentration en sodium, que nous observons également. Pour le calcium II, ils observent une diminution moins importante comparativement, ce qui correspond de même à nos courbes. De plus, si l'on compare les résultats trouvés de part et d'autre sur le cadmium I et II, on observe une très légère diminution du signal des deux raies, l'interférence restant relativement faible dans ce cas. Le fait que Fassel et coll. utilisent un système d'entraînement de l'aérosol différent de notre dispositif, constitué d'un pulvérisateur pneumatique sans désolvatation alors que nous utilisons un pulvérisateur ultrasonique associé à une désolvatation, nous suggère que cette similitude de résultats est due au plasma lui-même. On peut alors penser à une variation de la densité électronique due à la présence de sodium, mais comme nous l'avons déjà indiqué précédement sur le plasma fonctionnant à 5 MHz, cet élément n'a pas d'influence appréciable ni sur la densité électronique, ni sur la température. Nous avons vérifié ce fait à nouveau dans le cas du plasma à 40 MHz, en suivant l'évolution de la densité électronique à l'aide du couple de raies du magnésium I 285,2/II 279,6 (1 μg Mg ml^{-1}) et de la température sur les éléments excités à l'aide du couple de raies du titane II 322,2/II 322,4 (10 μg Ti ml^{-1}) en utilisant les valeurs de probabilité de transition citées préalablement [11]. Les résultats (Tableau 3) nous montrent que les deux paramètres température et densité électronique restent pratiquement constants: la variation de la température représente un écart maximum de 100 K (inférieur à l'incertitude de mesure), celle de la densité est négligeable. Ces deux paramètres pouvant être considérées comme constants, on ne peut

TABLEAU 3

Rapports des deux raies en fonction de la concentration en sodium

Concentration de Na (μg ml^{-1})	$\frac{\text{Mg I 285,2}}{\text{Mg II 279,6}}$	$\frac{\text{Ti II 322,2}}{\text{Ti II 322,4}}$
0	0,069	5,2
1	0,069	5,2
10	0,070	5,4
10^2	0,071	5,0
10^3	0,070	5,3

plus alors appliquer l'équation de Saha qui permet d'accéder aux densités des particules dans les différents états d'ionisation et par là à l'intensité des raies.

Néanmoins, nous pouvons avoir une idée de l'origine de ces variations. Comme nous l'avons indiqué, le phénomène ne provient vraisemblablement pas de la désolvatation. Il reste donc deux hypothèses possibles pour expliquer une telle interférence: soit une interférence d'atomisation, soit une interférence d'excitation. Pour lever le doute, nous avons cherché à distinguer ces phénomènes à l'aide de la spectroscopie d'absorption atomique en utilisant la méthode "à deux raies" précédemment décrite [8], sur le mélange calcium—sodium. Or en absorption atomique, nous avons constaté que les interférences subsistaient aussi bien sur les raies I (mesure Ca I 422,673; référence Ca I 430,253 nm) que sur les raies II (mesure Ca II 393,367; référence Ca II 396,847 nm). Il ne peut donc s'agir que d'une interférence d'atomisation et il est normal que l'on n'ait pas observé de variation significative de la densité électronique. Dans le cas particulier du mélange calcium—sodium, l'étude de l'influence de la variation de la puissance appliquée (Fig. 5) montre qu'au-delà d'une certaine puissance critique (2,0 kW) supérieure à la puissance utilisée dans les conditions de compromis de l'analyse (1,3 kW), l'interférence devient négligeable compte tenu de la précision des mesures. Nous avons vérifié que cela restait valable pour une puissance supérieure à la puissance critique quelle que soit la concentration en sodium.

Etude de l'influence du sodium sur l'intensité du phosphore

Si l'on étudie l'action importante du sodium sur le phosphore, le fait qu'elle ait lieu avec deux sources différents mais alimentées par le même système d'introduction des échantillons, nous a suggéré que ce type d'effet interéléments pouvait provenir du système d'introduction d'échantillons dans le plasma. Celui-ci est constitué d'un pulvérisateur ultrasonique associé à un système de désolvatation constitué d'un four et d'un réfrigérant. Afin de

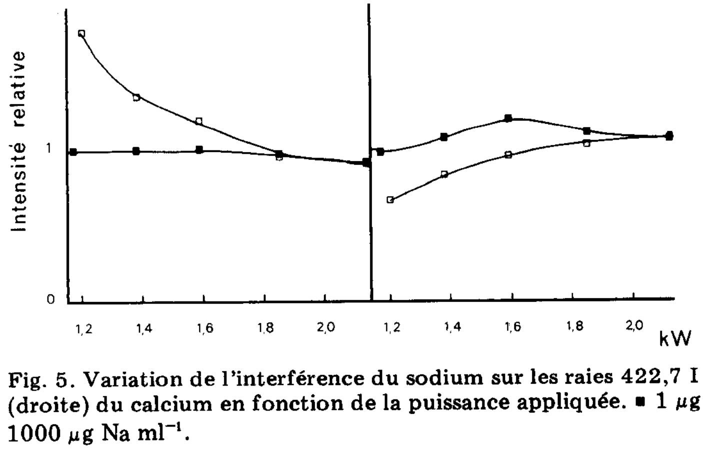

Fig. 5. Variation de l'interférence du sodium sur les raies 422,7 I (gauche) et 393,3 II (droite) du calcium en fonction de la puissance appliquée. ■ 1 μg Ca ml^{-1}. □ Ca + 1000 μg Na ml^{-1}.

déterminer l'influence de chacune des différentes parties de ce système, nous avons refait l'expérience, tout d'abord en ne faisant pas fonctionner le réfrigérant, ensuite en changeant le type de four, la température passant alors de 500 °C dans les expériences précédentes à 220 °C puis à 140 °C. Le phénomène ayant toujours lieu, nous avons fonctionné alors sans le système de désolvatation, le générateur utilisé supportant bien la présence d'eau. Les résultats représentés sur la Fig. 6 montrent qu'en l'absence de désolvatation, ce type d'interférence est alors supprimé.

Il avait déjà été constaté auparavant [12] que lors de la recondensation du solvant dans le réfrigérant, une certaine fraction de l'aérosol sec était entrainée (5 à 15 %), le pourcentage de l'entraînement variant en fonction de la nature du sel désolvaté. Dans le cas d'un mélange de plusieurs constituants, cela se traduit par des cinétiques de recombinaison avec le solvant qui peuvent être différentes, donc par des rapports de concentrations mesurées, différentes des rapports initiaux.

Dans le cas de l'effet du sodium (sous forme NaCl) sur le dosage du phosphore, l'étude a d'abord été faite en utilisant l'acide orthophosphorique (H_3PO_4). Nous avons pensé que la cinétique de resolvatation d'une liquide pouvait être très différente de celle d'un solide. Aussi avons-nous refait l'expérience en utilisant un sel restant solide à la température de fonctionnement du four: le pyrophosphate de sodium ($Na_4P_2O_7.10\ H_2O$; p.f. 880 °C). Nous avons adjoint l'étude d'un sel, le phosphate monosodique (NaH_2PO_4, H_2O) qui se décompose à 204 °C. Avec le pyrophosphate, l'interférence est supprimée. Avec le phosphate monosodique, la valeur de l'interférence dépend de la température du four: à 500 °C, elle est de 18 %, aux environs de 230 °C, elle n'est plus que de 7 %.

L'utilisation de la désolvatation présente l'avantage d'améliorer de façon sensible les limites de détection. Elle nécessite néanmoins la connaissance

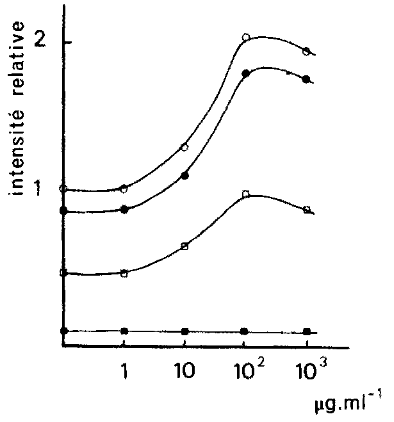

Fig. 6. Influence de la désolvation sur l'interférence de l'ion phosphate (50 $\mu g\ ml^{-1}$) par le sodium pour plusieurs températures du four. ○ 500 °C, ● 220 °C, □ 140 °C, ■ sans désolvatation.

précise des mécanismes physico-chimiques qui peuvent s'y manifester en fonction des différents éléments à analyser. La préparation des échantillons doit donc être conçue en fonction de ces impératifs.

CONCLUSION

Dans les conditions de travail de la spectrométrie d'émission utilisant comme source un générateur inductif de plasma, nous confirmons que les interférences sont faibles en général et qu'en particulier les interférences chimiques et les effets d'anions sont supprimées. Nous avons montré aussi que certains effets interéléments précédemment mentionnés étaient produits par le dispositif de désolvatation utilisé et pouvaient être supprimés en se passant de ce dispositif. Néanmoins, il peut subsister des interférences spectrales notamment dans le cas de matrices émettant un spectre riche tel que les éléments de transition (fer, par exemple). Enfin, certains effets interéléments ont été attribués à une interférence d'atomisation. Les propriétés de ce type d'interférence et le moyen de s'en affranchir restent actuellement à approfondir.

BIBLIOGRAPHIE

1 G. F. Kirkbright, A. F. Ward et T. S. West, Anal. Chim. Acta, 62 (1972) 241; 64 (1973) 353.
2 J. M. Mermet et J. Robin, Anal. Chim. Acta, 75 (1975) 271.
3 G. F. Larson, V. A. Fassel, R. H. Scott et R. N. Kniseley, Anal. Chem., 47 (1975) 238.
4 P. W. J. M. Boumans et F. J. de Boer, Spectrochim. Acta Part B, 30 (1975) 309.
5 C. C. Butler, R. N. Kniseley et V. A. Fassel, Anal. Chem., 47 (1975) 825.
6 G. R. Kornblum et L. de Galan, Actes XVIII. Colloq. Spectrosc. Intern. Grenoble, 2 (1975) 370.
7 R. L. Dahlquist et J. W. Knoll, Actes XVIII. Colloq. Spectrosc. Intern. Grenoble, 3 (1975) 679.
8 M. H. Abdallah, R. Diemiaszonek, J. Jarosz, J. M. Mermet, J. Robin et C. Trassy, Anal. Chim. Acta, 84 (1976) 267.
9 M. H. Abdallah, J. Jarosz, J. M. Mermet, C. Trassy et J. Robin, Actés XVIII. Colloq. Spectrosc. Intern. Grenoble, 3 (1975) 758.
10 G. R. Harrison, Wavelength tables, M.I.T. Press, Cambridge, Mass. U.S.A., 1969.
11 J. M. Mermet, Spectrochim. Acta Part B, 30 (1975) 383.
12 J. C. Souilliart, Thèse Lyon, 1972.

Analytica Chimica Acta, 87 (1976) 341—351

ANREICHERUNG VON ELEMENTSPUREN AUS HOCHREINEM GALLIUM DURCH PARTIELLES LÖSEN DER MATRIX. ANALYSE DES SPURENKONZENTRATS DURCH FLAMMEN-ATOMABSORPTIONS-SPEKTROMETRIE MIT DER "INJEKTIONSMETHODE"

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ZUSAMMENFASSUNG

Zahlreiche Elementspuren können auf einfache Weise aus hochreinem Galliummetall angereichert werden, indem man das Probenmaterial bis auf einen Rest von weniger als 5 mg in HCl/HNO_3 löst. Spuren, die elektrochemisch edler sind als die Matrix, (Ag, Au, Bi, Co, Cu, Fe, Hg, Ni, Pb, Pd und Sn) verbleiben bei diesem Prozeß mit Anreicherungsausbeuten > 95 % im Löserückstand. Dabei wird ein Anreicherungsfaktor von etwa 10^3 erreicht. Spuren Cd, Co, Fe, Tl und Zn können durch Behandeln der Galliumprobe mit einer Mischung von HJ und J_2 herausgelöst werden, ohne daß die Matrix selbst sich löst. Die Mehrzahl der angereicherten Elementspuren wird durch Flammen-AAS mit der "Injektionsmethode" bestimmt. Je nach Element werden Nachweisgrenzen ($3\ \sigma$) zwischen 0,06 und 0,004 p.p.m. erzielt. Die relative Standardabweichung liegt im allgemeinen um 5 %.

SUMMARY

Trace elements can be preconcentrated from high-purity gallium by simple dissolution of the sample in $HCl—HNO_3$ until a residue of less than 5 mg remains. Traces of metals which are nobler electrochemically than the matrix (Ag, Au, Bi, Co, Cu, Fe, Hg, Ni, Pb, Pd and Sn) are enriched in the residue (recovery > 95 %), a concentration factor of about 10^3 being obtained. Traces of Cd, Co, Fe, Tl and Zn can be extracted from gallium without dissolving the matrix by treatment with a mixture of HI and I_2. Most of the preconcentrated elements are determined by flame atomic absorption spectrometry with the "injection method". The limit of detection ($3\ \sigma$) for different elements was found to be between 0.06 and 0.004 p.p.m. The relative standard deviation is generally about 5 %.

Für die Bestimmung von Spurenverunreinigungen in Gallium-Metall werden heute vorwiegend spektrochemische Verfahren — die Emissionsspektralanalyse und die Massenspektrometrie — eingesetzt [1—4]. Zur Multi-Elementanreicherung haben sich vor allem Extraktionsverfahren bewährt, bei denen die Matrix aus salz-oder salpetersaurer Lösung mit Isopropyläther oder einem Alkylphosphat abgetrennt wird [1, 2, 5]. Die Reinheitskontrolle des Galliums erfordert insgesamt einen verhältnismäßig hohen manuellen und instrumentellen Aufwand. Umfangreiche Literaturhinweise über Verfahren zur Spurenbestimmung in Gallium sind unter [6, 7] zu finden.

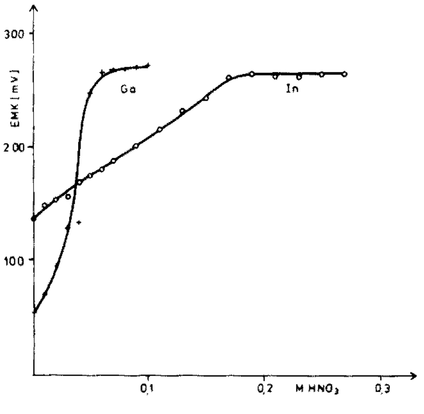
Im folgenden wird eine vom Prinzip her sehr einfache Methode beschrieben, bei der zahlreiche Elementspuren aus Gallium allein dadurch angereichert werden, daß man die Metallprobe bis auf einen geringen Rest in Säure löst Elemente, die elektrochemisch edler sind als die Matrix Gallium, verbleiben fast durchweg mit hoher Ausbeute im Löserückstand. Zusätzlich können einige unedlere Spuren durch Behandeln der flüssigen Galliumprobe mit verdünnter Säure abgetrennt werden, ohne daß sich störende Mengen des Matrixmetalls mit auflösen. Für die Analyse werden die Spurenkonzentrate auf ein kleines definiertes Volumen gebracht; die angereicherten Elemente werden mit Hilfe der "Injektionsmethode", einer Variante der Flammen-Atomabsorptions-Spektrometrie (AAS) bestimmt [8, 9]. In unserem Institut wird zur Zeit ein Verbundverfahren entwickelt, bei dem die aus hochreinem Gallium im Löserückstand konzentrierten Spurenverunreinigungen durch Emissionsspektralanalyse bestimmt werden. Über den Mechanismus, der die Spurenanreicherung beim partiellen Lösen metallischer Proben bestimmt, haben wir bereits im Zusammenhang mit der Analyse anderer Materialien ausführlich berichtet [10, 11]. Hier sollen deshalb nur die speziell bei der Galliumanalyse beobachteten Besonderheiten behandelt werden.

Eigenschaften und Verhalten der Matrix Gallium beim partiellen Lösen in Säure

Die für den Erfolg einer Spurenanreicherung nach unserem Verfahren wichtigen Eigenschaften des Galliums sind das verhältnismäßig niedrige elektrochemische Normalpotential ($E^\circ = -0{,}52$ V) und sein nur wenig oberhalb der Zimmertemperatur liegender Schmelzpunkt (Fp = 29,8 °C). Die Stellung von Spuren und Matrix in der Spannungsreihe bzw. die Größe und der Verlauf des Potentials der in Säure sich auflösenden Galliumprobe bestimmen in erster Linie, welche Elementspuren im Rückstand angereichert werden; der flüssige Zustand des Probenmaterials bewirkt, daß die an die Probenoberfläche gelangenden Spuren in der restlichen Metallmatrix gelöst bzw. von dieser benetzt und in elektrischem Kontakt mit dem Rückstand bleiben. Solange dieser Kontakt besteht, bestimmt die unedelste Komponente der Probe das Potential; nach kurzer Lösezeit ist dies stets die Matrix. Nur sie allein wird infolgedessen von der zugesetzten Säure angegriffen und aufgelöst; die edleren Elementspuren bleiben angereichert zurück.

Beim partiellen Lösen fester Metalle entstehen im allgemeinen Spurenverluste, da die edleren Bestandteile des Probenmaterials lediglich als lockerer Belag an der Oberfläche abgelagert werden. Von der Metallmatrix abfallende Partikel werden selbst potentialwirksam; sie lösen sich in der umgebenden Säure teilweise oder ganz auf: die darin enthaltenen Spuren gehen somit der Anreicherung verloren. Bei zahlreichen Matrixmetallen kann man Spurenverluste dieser Art jedoch wirksam verhindern, indem man die Proben vor dem Löseprozeß mit einem dünnen Quecksilberfilm überzieht und dadurch eine an der Oberfläche flüssige Metallphase erzeugt [10, 12, 13].

Das Potential von Gallium hängt wesentlich von der Art und Konzentration der zum Lösen verwendeten Säure ab; es ändert sich daher im Verlaufe des Löseprozesses. Lösegeschwindigkeit und Spurenausbeute werden unmittelbar vom Potential der Matrix beeinflußt. In halbkonzentrierter Salz- oder Salpetersäure löst sich reines Gallium z. B. nur sehr langsam auf; Salpetersäure bewirkt dabei eine beträchtliche Passivierung des Metalls. In Mischungen beider Säuren ist die Lösegeschwindigkeit merklich größer; das Ausmaß der Passivierung hängt auch hier vom HNO_3-Gehalt der Mischung ab. Abbildung 1 zeigt den Potentialverlauf des Galliums in 1 M Salzsäure mit ansteigendem Gehalt an Salpetersäure (Bezugselektrode bei allen Potentialmessungen: gesätt. Thalamid, Schott, Mainz, $E_B = -0.573$ V). Um den Einfluß der Zusammensetzung der Säure auf den durch partielles Lösen erzielbaren Trennerfolg zu zeigen, ist in das Diagramm der unter gleichen Bedingungen gewonnene Potentialverlauf für Indium mit eingezeichnet. Die bei beiden Metallen unterschiedliche Passivierung durch Salpetersäure führt dazu, daß das zunächst unedlere Gallium mit zunehmender HNO_3-Konzentration edler wird als Indium. Dementsprechend ist es nur in weitgehend salpetersäurefreier Salzsäure möglich, Spuren Indium im Löserückstand des Galliums anzureichern. Die Lösegeschwindigkeit in reiner HCl ist dabei allerdings für eine sinnvolle analytische Anwendung zu gering; andererseits wird Indium in HNO_3-haltiger HCl zusammen mit der Matrix Gallium aufgelöst. Ähnliche Abhängigkeiten kann man wohl auch für das Verhalten weiterer Elemente beim partiellen Lösen der Matrix Gallium annehmen. Abbildung 2 zeigt ergänzend den Potentialverlauf des Galliums bei Zusatz ansteigender Mengen Salpetersäure zu unterschiedlich konzentrierter Salzsäure: Bei gleicher HNO_3-Konzentration nimmt die Passivität erwartungsgemäß mit ansteigender HCl-



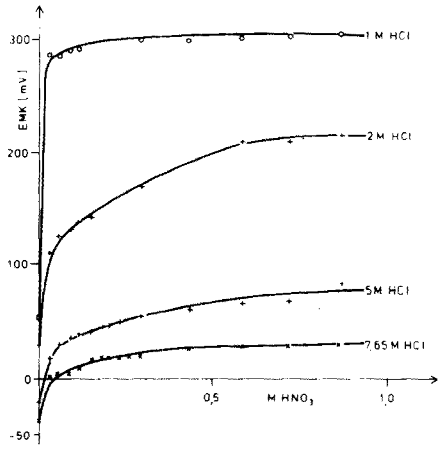


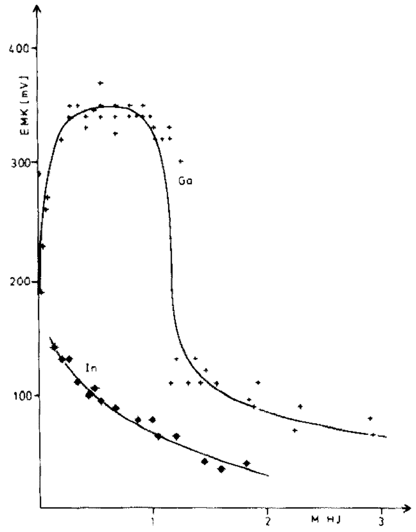
Abb. 1. Änderung des Potentials von 0,5 g Ga bzw. In in 1 M HCl mit unterschiedlichem HNO_3-Gehalt (Siedehitze).

Abb. 2. Änderung des Potentials von 0,5 g Ga in HCl/HNO_3-Mischungen unterschiedlicher Zusammensetzung (90 °C).

Konzentration ab. Zur gemeinsamen Anreicherung mehrerer Elementspuren durch partielles Lösen der Matrix muß das Potential möglichst niedrig gehalten werden; nach Aussage dieser Versuche ist es deshalb zweckmäßig, mit Säuremischungen von hoher HCl-, aber niedriger HNO_3-Konzentration zu arbeiten. 5—6 M Salzsäure erzielt die geringste Lösezeit für Gallium, wenn sie gleichzeitig etwa 0,15 M an HNO_3 ist.

Völlig anders müssen die Bedingungen gewählt werden, wenn unedlere Elementspuren durch eine Säurebehandlung aus der Galliumprobe herausgelöst werden sollen, ohne daß zugleich größere Mengen der Matrix mit aufgelöst werden. Hier darf die Lösegeschwindigkeit für die Matrix bei gleichzeitig hoher Passivierung des Galliums nur sehr gering sein, damit möglichst viele Spuren erfaßt, aber ein weitgehend matrixfreies Spurenkonzentrat erhalten wird. Sehr verdünnte HCl/HNO_3-Mischungen oder reine verdünnte HNO_3 führen hier nicht zum Ziel, da auf den Galliumproben Oberflächenbeläge entstehen, die das Herauslösen der Spuren behindern. Bessere Ergebnisse werden mit jodhaltiger Jodwasserstoffsäure erhalten. In Abb. 3 ist der Potentialverlauf von Gallium und Indium in HJ von ansteigender Konzentration dargestellt.

Interessant ist das Potentialmaximum des Galliums in der abgebildeten Kurve. Wir nehmen an, daß der Kurvenverlauf durch eine Passivierungsschicht an der Probenoberfläche verursacht wird, für deren Zustandekommen der geringe J_2-Eigengehalt der Säure verantwortlich ist. Mit zunehmender Acidität



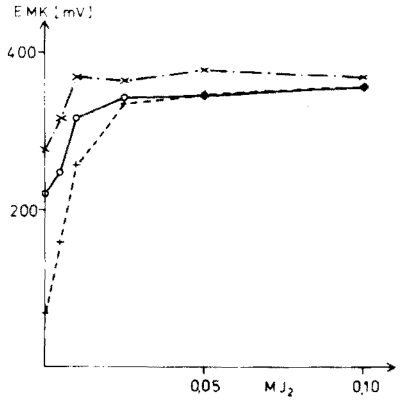


Abb. 3. Änderung des Potentials von 0,5 g Ga bzw. In in HJ unterschiedlicher Konzentration (90 °C).

Abb. 4. Änderung des Potentials von Ga in 0,5 M HJ mit unterschiedlichem J_2-Gehalt (90 °C). × 0,55 g Ga. ○ 2,2 g Ga. + 5,5 g Ga.

der eingesetzten Säure wird diese Schicht aufgelöst; die Passivität nimmt wieder ab. An Indiumproben treten solche Schichten nicht auf, vermutlich wegen der Bildung stabiler Jodokomplexe dieses Elements: die Passivierung bleibt deshalb auch in verdünnter Säure aus. Beim Auflösen von Gallium in HJ/J_2 wird das Jod an der Oberfläche der Metallprobe reduziert; die zunächst braune Jodwasserstoffsäure entfärbt sich. Die Dauer der Passivierung hängt insgesamt vom Jodgehalt der Säure, von ihrer Acidität und, wie weitere Versuche ergaben, auch von der eingesetzten Galliummenge ab. Durch Proben mit größerer Oberfläche wird der vorhandene geringe Jodgehalt der Säure offensichtlich so rasch "verbraucht", daß als Folge davon die erwünschte starke Passivierung fast ganz ausbleibt. Sie wird bei hohen Galliumeinwaagen erst dann erreicht, wenn man der Jodwasserstoffsäure über den Eigengehalt hinaus weiteres Jod zusetzt (Abb. 4).

SPURENANREICHERUNG DURCH PARTIELLES LÖSEN VON GALLIUMPROBEN

Wie Vorversuche zeigten, werden Zahl und Ausbeute der im Löserückstand angereicherten Elemente von der eingesetzten Säure bzw. Säuremischung beeinflußt. Zur Ermittlung günstiger Arbeitsbedingungen mußte deshalb der Verbleib aller in die Untersuchungen einbezogenen Spuren beim partiellen Lösen des Galliums überprüft werden. Um Proben mit definierten Spurengehalten herzustellen, wurden die Elemente Ag, Au, Bi, Cd, Co, Cu, Fe, Hg, In, Ni, Pb, Pd, Sn, Tl und Zn in Nano- bis Mikrogramm-Mengen aus 2 M salzsaurer (bei Ag schwefelsaurer) Lösung elektrolytisch an eingewogenem Galliummetall (99,9999 % Ga) abgeschieden. Die Vollständigkeit der Abscheidung wurde nach Beendigung der Elektrolyse durch Analyse der dekantierten Säure kontrolliert; bei unvollständiger Abscheidung wurden die Spurengehalte der Proben korrigiert.

Zur Anreicherung von Ag, Au, Bi, Cd, Co, Cu, Fe, Hg, In, Ni, Pb, Pd, Sn, und Tl

Die mit Spuren dotierten Galliumproben (0,5—5 g Ga) wurden in HCl/HNO_3-Mischungen unterschiedlicher Konzentration und Zusammensetzung bis auf einen Rest von jeweils etwa 2—5 mg Ga gelöst. Zur Erhöhung der Lösegeschwindigkeit wurde dabei bis nahe zum Sieden erhitzt. Der Löserückstand wurde in Königswasser gelöst, auf ein definiertes Volumen gebracht und mit Hilfe der AAS analysiert. Das Verhalten von Spuren Sn wurde nur in wenigen Versuchen überprüft. Da Sn bei der beschriebenen Behandlung als Zinnstein ungelöst bleibt, wurde der Rückstand des Galliums für diese Versuche in konzentrierter Schwefelsäure gelöst. Die angereicherten Zinnspuren wurden nach extraktiver Abtrennung von störenden Begleitelementen photometrisch mit Hämatein bestimmt [14, 15].

Die nach Löseverhalten und Spurenausbeute günstigsten Ergebnisse erhält man bei Verwenden einer Säuremischung, die 3 M an HCl sowie 0,15 M an HNO_3 ist (100 ml 3 M HCl + 1 ml 65 % ige HNO_3). Von den eingesetzten Elementspuren werden lediglich Cd, In und Tl nicht oder mit nur geringer

TABELLE 1

Ergebnisse der Spurenanreicherung durch partielles Lösen der Matrix Gallium in HCl/HNO$_3$ nach Arbeitsvorschrift A

Element Me	Galliumeinwaage (g)	Eichumfang (p.p.m.)	Me angereichert (%)	rel. Standardabweichung ($N = 10$)		Nachweisgrenze (p.p.m.)
				(%)	gemessen bei (p.p.m.)	
Ni	5	0,02– 25	> 95	4,7	0,10	0,02
Pb	5	0,02– 25	> 95	6,5	0,13	0,02
Fe	5	0,02– 25	> 95	6,2	0,11	0,02
Bi	5	0,1 – 25	> 95	4,4	0,11	0,06
Cu	5	0,01– 10	> 95	2,6	0,13	0,009
Pd	5	0,05– 25	> 95	2,5	0,10	0,05
Au	5	0,04– 50	> 95	4,1	0,11	0,04
Co	1	10 – 50	> 95			
Sn	1	1 –100	> 95			
Ag	1	0,1 – 1,5	> 95	4,5	1,1	0,05
Hg	1	0,1 – 50	> 95	2,9	1,4	0,02
Cd	1	1 – 10	< 5			
In	1	5 – 50	etwa 30			
Tl	1	5 – 50	< 5			

Ausbeute im Löserückstand wiedergefunden; die übrigen Spuren gelangen zu mehr als 95 % der vorgegebenen Menge ins Spurenkonzentrat (Tab. 1). Ursache für die Minderbefunde bei diesen gegenüber Gallium dem Normalpotential nach nur geringfügig edleren Elementen ist wohl vor allem die bereits diskutierte Passivierung des Galliums in der zum Lösen verwendeten Säure. Durch die Potentialerhöhung wird die Matrix edler als diese Spuren; sie werden deshalb gleichzeitig mit der Matrix oder sogar bevorzugt aufgelöst. Die Passivierung der Probe scheint in gleicher Weise auch das Verhalten von Spuren Kobalt zu beeinflussen: Co wurde nur dann mit hoher Ausbeute im Rückstand wiedergefunden, wenn es zu mehr als etwa 10 p.p.m. im Gallium enthalten war; bei geringeren Gehalten waren die Ausbeuten deutlich geringer. Eine Überprüfung dieser Ergebnisse mit Galliumproben unterschiedlicher Einwaage zeigte, daß offensichtlich immer eine annähernd gleiche Menge Kobalt zusammen mit der Matrix aufgelöst wird; die Ausbeute für das im Löserückstand angereicherte Kobalt wird dadurch umso kleiner, je geringer der tatsächliche Kobaltgehalt der Galliumprobe ist. Die dem Löserückstand verloren gehende Kobaltmenge nimmt zu, wenn die Probeneinwaage erhöht wird.

Arbeitsvorschrift A: Das Gallium (5 g) wird in 300 ml einer Säuremischung (3 M HCl – 0,15 M HNO$_3$) bei 90–95 °C bis auf einen Rückstand von weniger als 5 mg Ga gelöst. Die überstehende Lösung wird dekantiert, der Gallium-Rückstand wird im Becherglas mit Wasser, dann mit wenig Aceton gespült. Nach Verdunsten des Acetons wird soweit abgekühlt, bis die Galliumkugel fest geworden ist; sie wird in einen 1 ml-Meßkolben überführt, mit 90 μl 36 %iger HCl und 30 μl 65 %iger HNO_3 versetzt und unter Erwärmen gelöst. Die Lösung wird bis fast zur Trockne eingeengt (Heizplatte und Oberflächenstrahler). Nach dem Erkalten wird mit 2 M HNO_3 bis zur Marke aufgefüllt. In dieser Lösung werden Ag, Au, Bi, (Co), Cu, Fe, Hg, Ni, Pb and Pd durch AAS bestimmt.

Zur Anreicherung von Cd, Co, Fe, In, Tl und Zn

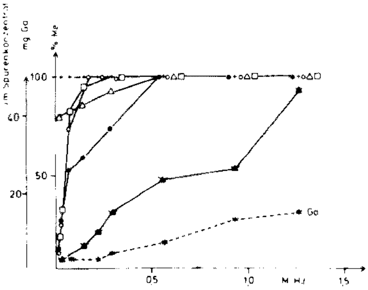
Bei Gallium als flüssigem Probenmaterial gelingt es leicht, durch Erhitzen in verdünnter Salzsäure (1 M HCl, 10 min Siedehitze) p.p.m.-Mengen Zink in wenigen Minuten quantitativ herauszulösen, ohne daß größere Mengen der Matrix mit aufgelöst werden. Nicht so vollständig gelang die Abtrennung der Spuren Al, Ca, Mg und Mn; die Ursachen dafür wurden bisher nicht näher untersucht. Die in jodhaltiger Jodwasserstoffsäure beobachtete starke Passivierung und Potentialerhöhung von Gallium deuten Möglichkeiten zur Anreicherung auch edlerer Spurenmetalle nach diesem Verfahren an. Voraussetzung für die Anreicherung von Elementen, die dem Normalpotential nach edler sind als Gallium, ist jedoch, daß sie, anders als die Matrix, im Löseprozeß nicht oder nur geringfügig passiviert werden. Unter diesem Gesichtspunkt wurde das Verhalten von Spuren Cd, Co, Fe, In und Tl überprüft.

Auch bei diesen Versuchen zeigte sich der Einfluß der eingesetzten Galliummenge auf die Güte der Trennung. Aus etwa 0,5 g Gallium konnten z.B. 5 μg der Elemente Cd, Co, Fe, Tl und Zn bereits in wenigen Minuten mit Ausbeuten $>$ 95 % herausgelöst werden, wenn die Proben in 5 ml 0,5 M HJ, die durch J_2 schwach braun gefärbt war, auf 95—100 °C erhitzt wurden. Spuren Indium wurden dabei nur teilweise erfaßt; Indium geht in merklichen Mengen erst dann in Lösung, wenn auch die Matrix Gallium sich aufzulösen beginnt (Abb. 5). Entsprechende Versuche mit Einwaagen von 5 g Gallium führten bei Spuren Cd, Tl und Zn wiederum zum Erfolg; Co und Fe wurden dagegen zu höchstens 60 % der eingesetzten Menge angereichert, auch wenn Lösezeit, Säuremenge und -konzentration erhöht wurden. Zusätze von J_2 verbesserten das Ergebnis zwar etwas, gleichzeitig wurde jedoch auch die Matrix verstärkt aufgelöst. Unter den Bedingungen der Arbeitsvorschrift gelangen etwa 10 mg Ga ins Spurenkonzentrat.

Arbeitsvorschrift B: Das Gallium (5 g) wird in einem 25-ml Teflonbecher 15 min mit 5 ml Jod—Jodwasserstoffsäure (0,2 M HJ—0,05 M J_2) in der Siedehitze behandelt. Die Säure wird anschließend von der Metallprobe dekantiert und in einem weiteren 25-ml Teflonbecher bis fast zur Trockne eingeengt. Der Rückstand wird mit 2 M HNO_3 aufgenommen, in einen 2 ml-Meßkolben übergespült und zur Marke aufgefüllt. In dieser Lösung werden Cd, Tl und Zn durch AAS bestimmt. Bei Einwaagen bis zu 0,5 g Gallium werden zusätzlich Co und Fe erfaßt.

ZUR AAS-BESTIMMUNG VON ELEMENTSPUREN IN GALLIUM; ANALYSE DER SPURENKONZENTRATE

Die Bestimmung von Elementspuren durch Flammen-AAS wird in Lösungen mit hohen Gallium-Konzentrationen beträchtlich gestört: Man erhält verminderte Elementsignale auf einem starken Untergrund an nichtspezifischer Absorption. Lediglich in Lösungen mit Galliumgehalten unterhalb von etwa 5 mg Ga ml^{-1} kann mit unverminderter Empfindlichkeit und — bei Verwenden eines Untergrundkompensators — praktisch störungsfrei gemessen werden (Abb. 6). Besonders wichtig ist der Kompensator für die Bestimmung aller Elemente, deren Resonanzlinie in den Bereich von 210 bis 290 nm fällt. Wie Messungen zeigten, treten in diesem Bereich intensive Molekülbanden auf, die dem GaCl zugeschrieben werden [16] (Abb. 7).



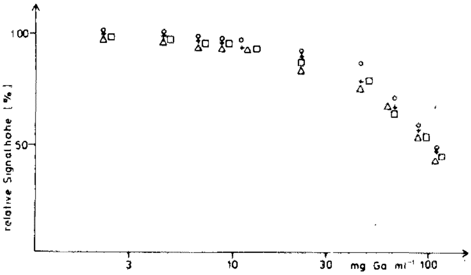


Abb. 5. Anreicherung von Spuren Me durch Behandeln der Galliumprobe (0,5 g Ga) mit verdünnter HJ unterschiedlicher Konzentration (10 min.; Siedehitze). +Zn. ○Cd. △Tl. ✱ In. □ Co. ● Fe.

Abb. 6. Einfluß der Galliumkonzentration der Meßlösung auf die Größe des Absorptionssignals von Spuren Cu, Zn, Pb (je 1 p.p.m.) und Bi (5 p.p.m.). +Zn. ○Pb. △Bi. □Cu.

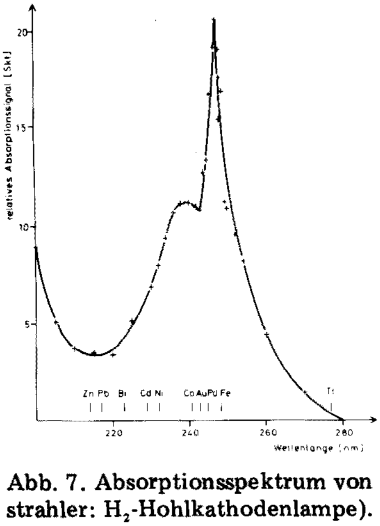


Abb. 7. Absorptionsspektrum von GaCl in der Acetylen-Luft-Flamme (Hintergrundstrahler: H_2-Hohlkathodenlampe).

Um die angereicherten Elemente nachweisstark zu bestimmen, haben wir das Meßvolumen des Spurenkonzentrats so klein wie möglich gewählt. Optimal wäre ein Probenvolumen, das zur Bestimmung aller enthaltenen Elemente gerade ausreicht, wobei das Spurenkonzentrat gleichzeitig noch so verdünnt ist, daß Störungen durch Reste der Matrix vermieden werden. Bei Verwenden der "Injektionsmethode", einer für die Analyse kleiner Substanzmengen sowie für die Multi-Elementanalyse von Spurenkonzentraten interessante Variante der Flammen-AAS, gelingt es problemlos, etwa 10 Elemente aus insgesamt 1 ml Probenlösung nacheinander zu messen [8, 9].

Nach diesem Verfahren werden für jede Bestimmung 50—100 μl-Anteile der Probenlösung mit einer Mikroliter-Kolbenpipette über einen kleinen Trichter in das Zerstäuber-Brenner-System des AAS-Gerätes injiziert. Bei günstig gewählten Meßbedingungen (Saugleistung des Zerstäubers, Ansprechzeit des Meßsystems) erhält man Analysensignale in Form von Extinktionsspitzen, deren Höhe nur wenig kleiner ist, als die der stationären Signale, die man bei üblicher Arbeitsweise mißt. Nähere Einzelheiten sind den zitierten Arbeiten zu entnehmen.

Apparative Angaben: Atomabsorptions-Spektrometer Varian Modell 1000 mit Untergrundkompensator BC 6 und Millivolt-Schreiber. Luft-Acetylen-Flamme. Ansaugrate: etwa 5 ml min^{-1}; Dämpfungszeitkonstante: 0,3 s (Stufe 1); Injektionsvolumen: 50 μl für jede Bestimmung. Zur Bestimmung des Quecksilbers wurde das erstmals von Poluektov und Vitkun [17] sowie von Hatch und Ott [18] beschriebene flammenlose Verfahren benutzt. Bei dieser Anordnung wird das Quecksilber mit $SnCl_2$ zum Metall reduziert und anschließend im Luftstrom durch eine im Strahlengang des AAS-Gerätes befindliche Quarzküvette geleitet. Umfassende Literaturangaben zu diesem Verfahren siehe [19, 20].

Arbeitsvorschrift: In das Reaktionsgefäß werden 5 g $SnCl_2 \cdot 2\,H_2O$ sowie 1 ml 10 %ige HCl gegeben. Die Suspension wird mit einem Magnetrührer intensiv gerührt, während ein gleichmäßiger Luftstrom hindurchgeleitet wird, der das als Verunreinigung in den Reagenzien enthaltene Quecksilber austreibt. Die Reinigung ist beendet, wenn das Absorptionssignal des Quecksilbers die Grundlinie erreicht. Zur Bestimmung werden 50 μl der Probenlösung verwendet. Bei abgeschaltetem Luftstrom wird etwa 1 min intensiv durchmischt; dann wird das Quecksilber im Luftstrom (etwa 1,5 l min^{-1}) durch die Quarzküvette geleitet. Das Absorptionssignal wird registriert. Entsprechend dieser Vorschrift wird das Verfahren mit Hg-Spurenlösung in 2 M HNO_3 geeicht. Die $SnCl_2$/HCl-Suspension wird jeweils nach 15 Analysen erneuert.

Apparative Angaben: Atomabsorptions-Spektrometer Perkin-Elmer Modell 300 mit Untergrundkompensator und Millivolt-Schreiber. Hg-Reaktionseinrichtung: 25 ml-Reaktionsgefäß mit Gaseinleitungsrohr und Dreiwegehahn; Quarzküvette (l = 17,2 cm; ϕ = 1,4 cm); Membran-Luftpumpe.

ERGEBNISSE

Die Ergebnisse unserer Untersuchungen sind in den Tabellen 1 und 2 zusammengefaßt. Für die Bestimmung der relativen Standardabweichung wurden jeweils 10 Galliumproben mit den in den Tabellen angegebenen Spurengehalten analysiert. Die Nachweisgrenzen (3 σ-Grenzen) wurden aus den Streuungen des Untergrundes bei der Analyse von Reinst-Gallium (99,9999 % Ga) errechnet.

TABELLE 2

Ergebnisse der Spurenanreicherung durch Behandeln der Matrix Gallium mit HJ/J_2 nach Arbeitsvorschrift B

Element Me	Gallium-einwaage (g)	Eichumfang (p.p.m.)	Me angereichert (%)	rel. Standardabweichung (N = 10)		Nachweis-grenze (p.p.m.)
				(%)	gemessen bei (p.p.m.)	
Cd	5	0,01— 1	> 95	4,6	0,88	0,004
	0,5	0,1 — 10	> 95			
Tl	5	0,2 — 10	> 95	4,0	0,85	0,06
	0,5	1 — 50	> 95			
Zn	5	0,05— 20	> 95	5,5	0,30	0,004
Co	5	0,2 — 10	etwa 60[a]			
	0,5	1 —100	> 95			
Fe	5	0,1 — 5	etwa 60[a]			
	0,5	1 —100	> 95			

[a] Wenig reproduzierbare Werte.

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LITERATUR

1 E. B. Owens, Appl. Spectrosc., 13 (1959) 105.
2 J. H. Oldfield und E. P. Bridge, Analyst, 86 (1961) 267.
3 M. S. Wang, Appl. Spectrosc., 24 (1970) 60.
4 M. Nalbantoglu, in W. L. Mead (Ed.), Advances in Mass Spectrometry, Vol. 3, Elsevier, Amsterdam, 1966.
5 V. G. Goryushina und E. Y. Biryukova, Zh. Anal. Khim., 24 (1969) 580.
6 A. M. Dymov und A. P. Savostin, Analytical Chemistry of Gallium, Ann Arbor Science Publ., Ann Arbor, Michigan, 1970.
7 I. P. Alimarin (Ed.), Analysis of High-purity Materials, Israel Program for Scientific Translations, Jerusalem, 1968.
8 E. Sebastiani, K. Ohls und G. Riemer, Z. Anal. Chem., 264 (1973) 105.
9 H. Berndt und E. Jackwerth, Spectrochim. Acta Part B, 30 (1975) 169.

10 E. Jackwerth, E. Döring, J. Lohmar und G. Schwark, Z. Anal. Chem., 260 (1972) 177.
11 R. Höhn, Dissertation, Bochum, 1975.
12 E. Jackwerth, R. Höhn und K. Koos, Z. Anal. Chem., 264 (1973) 1.
13 R. Höhn, E. Jackwerth und K. Koos, Spectrochim. Acta Part B, 29 (1974) 225.
14 E. Asmus, H. J. Altmann und E. Thomasz, Z. Anal. Chem., 216 (1965) 3.
15 D. Gilbert und E. B. Sandell, Microchem. J., 4 (1960) 491.
16 R. W. B. Pearse und A. G. Gaydon, The Identification of Molecular Spectra, Chapman and Hall, London, 1950.
17 V. S. Poluektov und R. A. Vitkun, Zh. Anal. Khim., 18 (1963) 33.
18 W. R. Hatch und W. L. Ott, Anal. Chem., 40 (1968) 2085.
19 A. M. Ure, Anal. Chim. Acta, 76 (1975) 1.
20 S. Chilov, Talanta, 22 (1975) 205.

Analytica Chimica Acta, 87 (1976) 353—363

FLOW INJECTION ANALYSIS
PART VI. THE DETERMINATION OF PHOSPHATE AND CHLORIDE IN BLOOD SERUM BY DIALYSIS AND SAMPLE DILUTION

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SUMMARY

The rapid determination of chloride and inorganic phosphate in blood serum based on continuous flow spectrophotometry was adapted to Flow Injection Analysis by applying dialysis as well as differential dilution of the injected samples. In addition to the manual injection procedure, an automated microsampling unit was developed and used. By continuous dialysis, chloride could be determined reproducibly at a sampling rate of 125 samples per hour at sample volumes of 60 μl or less. A similar sampling rate and high precision were obtained for the determination of inorganic phosphate by using differential dilution.

The practical applications of the Flow Injection method [1—6] have so far been limited mainly to samples of agricultural origin. Clinical analysis, however, is another area where the advantages of this new technique, i.e. simplicity, speed and high sampling rates, would be useful. In contrast to soil and plant analyses, the materials for clinical analysis are more uniform, and, indeed, most of the analyses are performed on blood serum. This does not, however, imply that the actual analyses are simpler to execute, as several important requirements have to be fulfilled. First, the amount of sample material available is often limited, and the samples of serum differ from the aqueous standards used for calibration in many respects; consequently, a systematic error is frequently inherent in the analyzer used. Furthermore, either dialysis or sample dilution is often required to eliminate the interference of proteins and other large molecules, or to accommodate the signal within the range of the detector. Last but not least, proteins and fats tend to deposit in the conduits of the analyzer, flow cells, etc., and therefore the chemistry must be designed so that effective washout is achieved.

Consequently, the Flow Injection Analyzer for the clinical laboratory must be able to handle any sample volume between 200 and 20 μl, and because of the large work load, the injection of samples should be automated. Dialysis should not alter the geometry of the sample plug formed by the action of injection, i.e. the dialyzed material should form an identical, yet diluted and protein-free sample plug on the other side of the membrane, proceeding along with the recipient stream. The automated sample dilution must extend even to the range of 1:100 with a reproducibility of repeated injection of 1 % or better. It was decided to develop these techniques and to test them on determination of inorganic phosphate and chloride in blood serum, as these chemistries have been previously used successfully in the Flow Injection system, and also because these two species represent two concentration extremes in blood analyses (ca. 100 meq l^{-1} for chloride, and 3.5 mg P/100 ml for phosphate in normal serum). Besides, both these determinations are usually performed on dialysed serum samples [7—9].

EXPERIMENTAL

Reagents

The composition of the reagents has been described previously [3, 5], and the chemistries are designed on the basis of routine AutoAnalyzer procedures [8, 9]. In order to obtain a uniform flow and to even out the mixing irregularities which might occur because of the difference in the surface tension of water and serum, a number of surfactants (Brij-35, Levor IV, and Wetting Agent FC-134, all from Technicon) as well as a non-ionic detergent (Detergol Triplex, Struers A/S, Denmark) were added to the reagents in concentrations ranging from 0.05 to 2 %. Unfortunately, all of them seemed to induce coagulation of proteins, which manifested itself by a continuous increase in the baseline signal and by changing the effectiveness of dialysis. However, addition of 1 % glycerin to all reagent solutions ensured smooth mixing and a reliable washout.

Standards

The aqueous chloride and phosphate standard solutions were prepared by dissolution of sodium chloride and potassium dihydrogenphosphate, respectively, in distilled water.

The serum standards were serum pool (University Hospital of Copenhagen) and four commercially available freeze-dried sera: Technicon SMA Reference Serum 2; Moni-trol I and II (DADE); and Auto-Ref (DADE). Each serum was dissolved in the solvent supplied with the serum and prepared according to the manufacturer's instruction.

Instruments

The peristaltic pump, a Technicon AutoAnalyzer model II, was initially geared up so that the speed of delivery was exactly doubled. As the work progressed, however, and the analyzer became more compact, lower pumping rates were adopted, and therefore the final versions of the manifolds used can very well be operated by a normally geared pump or any other pump with similar characteristics. The spectrophotometer was a Beckman model DB-GT, equipped with a Helma flow-cell type 178-QS (volume 80 μl, light path 10 mm), used in combination with a Radiometer Servograph recorder furnished with a multirange high-sensitivity REA input unit. Here the important requirement for the detector and readout unit is that the recorder has a fast response. Use of flow cells of extremely small volume, e.g. 5 μl as in the Technicon SMAC system [10], is unnecessary for the Flow Injection system as the stream of all combined solutions is sufficient to ensure a complete washout of the detector and thus complete the return of the signal to the baseline.

The Flow Injection Analyzer consisted, besides the units mentioned above, of a manifold assembled on top of a water bath (Fig. 1). Polyethylene tubing (1.00, 0.75 and 0.50 mm i.d.) was used for making mixing coils, transmission, reagent and waste lines. Fittings were made from Perspex blocks furnished with conical, internally polished holes, into which polyethylene tubes of different i.d. but approximately the same o.d. fitted self-lockingly. This, and the fact that the whole manifold was assembled by means of Lego building blocks, made the reprogramming easy and the whole system inexpensive. Line lengths could be tailored exactly to the speed of mixing and reaction time, and thus kept at an absolute minimum.

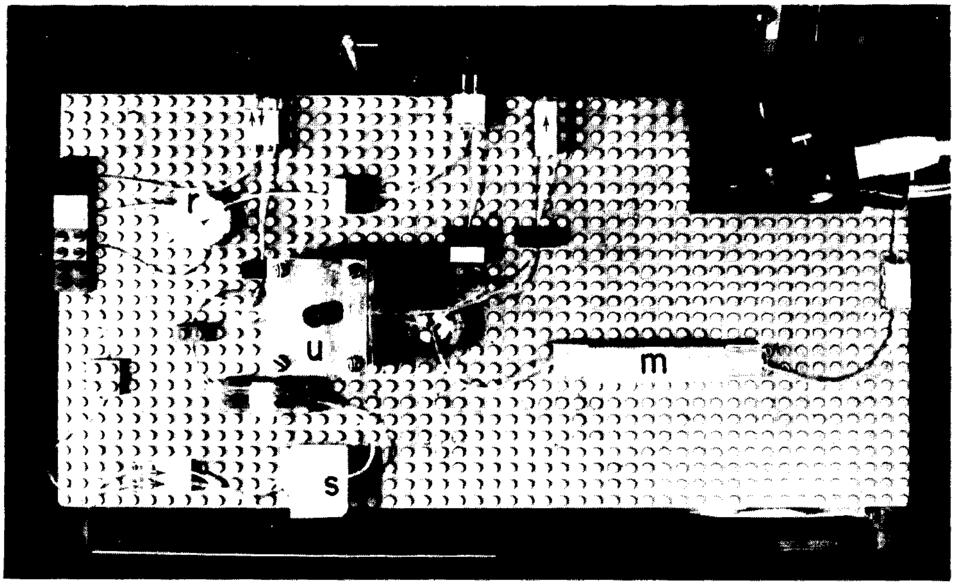


Fig. 1. Manifold of the Flow Injection Analyzer, comprising injection block (s), dialyzer (u), mixing coil for colour forming reaction (m), and a thermostated water bath in which coils for preheating of reagents are submerged. All tubes used are of 1.00 mm i.d. unless otherwise stated in the text.

Sampling. The sampling was done in two ways: by manual injection with a polypropylene syringe through a minivalve of the flap type [2—5], or semi-automatically through a sampling loop which was controlled by two magnetic valves which synchronously opened and closed two pairs of tubes (a—c, a′—c′) and (b—c, b′—c′), Fig. 2. The advantage of the manual injection is its simplicity, and as long as sufficient sample material is available and the number of samples to be injected is limited, this procedure is preferable. Disposable syringes of 1-ml capacity are, however, obviously not accurate enough for injections of samples smaller than 200 μl, and although the use of spring-loaded micro syringes was considered, an automated injection system in which the amount of sample can be widely varied by changing the volume of the sampling loop was finally designed.

The sample is aspirated from the sampler cup (S) into the loop by the pump and its excess is put to waste (W). During the sampling cycle tubes a—c are opened and b—c closed and therefore the carrier stream C bypasses through coil B into the manifold (M). When the loop has been filled, the b—c lines are opened and a—c closed and as the coil (B) is designed so that it has a much higher flow resistance than the loop, the sample is injected into the carrier stream line as a well defined plug. Changing the length and i.d. of the sampling loop, which is made of polyethylene tubing, and of bypass coil B is very simple, as the sampler is built on the same principle as the manifold. The versatility of the sample loop and its adaptability to fully automated sampling by combining it with a sample carousel, which would also provide synchronized impulses for the magnetic valves, is obvious. In addition, because of the damping action of the bypass coil, the sudden forward movement of the carrier stream, which is a characteristic of the manual injection, does not occur. Therefore several samples can be introduced into the carrier stream at close intervals without serious disturbance of the flow parameters, should a slower chemical reaction require a long line length. Finally, reproducible injection of microvolumes is not only important

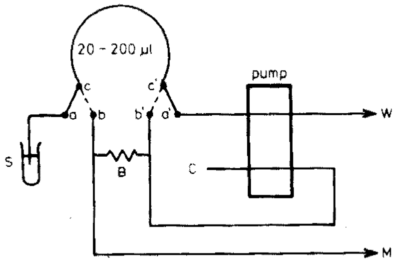


Fig. 2. Automated injection system with a sample loop. S, sample loop, exchangeable according to the volume of sample to be injected; B, bypass coil (1.2 m long, 0.5 mm i.d.); C, carrier stream; M, manifold; W, waste. a—c, a′—c′, c—b and c′—b′ are connections which are closed and opened synchronously by a pair of magnetic valves.

from the viewpoint of economy of sample material, but allows an automated dilution of the sample material, which is often required.

Dialyzers. Two units were used, a short one for the chloride system and a long for the phosphate system. Each dialyzer was machined from two Perspex blocks, 30 × 15.5 mm, with lengths of 43 mm and 100 mm, respectively, for the two systems. Each block was furnished with a straight groove of half-elliptic cross-section, 1.40 mm wide and 0.8 mm deep. From both ends of each groove, a 1-mm i.d. hole was drilled at an angle of approximately 45° towards and through the outer sides of the Perspex blocks, the outer orifices being conical so that the transmission lines could be inserted in the usual manner. Thus the dialysis path of the short dialyzer was 20.0 mm, having a total surface area of 28 mm^2, while the long dialyzer had a path of 75 mm and a surface area of 105 mm^2. When the assembly was mounted, the dialysis membrane (Technicon Type C, or Cuprophan Type 150 PM, Enka Glanzstoff AG, Germany) was gently stretched between the blocks which were then, being precisely aligned by two pins, pressed together by an adjustable clamp. Although dialyzers of longer dialysis paths were made and tested for each system, variation of the pumping rates of the carrier and recipient streams proved to be the most practical way of adjusting the yield of dialysis and thus the sensitivity of the determination (see also Fig. 4).

Dialysis and dilution

Continuous dialysis plays an important role in automated chemical analysis and is often said to be indispensable. Thus proteins interfere in the determination of chloride in serum, as they react with the colour-forming reagent leading to high results [7]. In the determination of inorganic phosphate, organically bound phosphate might also react resulting in the formation of a blue colour [7]. Besides, as mentioned above, protein deposits in the conduits can prove troublesome. As the efficiency of the dialysis on the continuously moving stream is only about 1—4 %, the dialyzer serves not only as a separator, but also as an effective dilutor. The yield of the continuous dialysis depends on the membrane area, residence time of the sample and mixing, and therefore on pumping rates, temperature, membrane thickness, concentration of solutions, and their viscosity; thus, all these factors must be carefully controlled, if optimal reproducibility is to be achieved. For this reason there is a tendency in clinical chemistry to avoid dialysis whenever possible [11] and replace it by dilution, supplemented if necessary by blanking. Introduction of small sample volumes which are diluted in the analyzer allows the level of the analyte to be adjusted to match the detector range, and decreases the amount of coagulable materials introduced into the system.

RESULTS

Determination of chloride

The determination of chloride was tested over a number of stages which involved continuous dialysis (Fig. 3a) with both manual and automated injection, as well as differential dilution of small volumes of sample injected automatically into the system (Fig. 3b). The resulting manifolds, reagent concentrations and pumping rates were devised through experiments aimed at finding the highest sampling rate and minimum reagent consumption per assay. For the dialysis, the Cuprophan membrane (Type 150 PM) was adopted as it was as satisfactory as other membrane materials, although it was the cheapest. As an example of one of the parameters tested, the influence of the residence time of the sample plug in the short dialyzer is shown in Fig. 4. Predictably, the second most influential factor, as was proved experimentally for both the long and the short dialyzer, was the area of the dialysis membrane exposed to the donor stream. Temperature and acid concentration of the donor stream had much less influence on the effectiveness of the dialysis, yet had to be controlled in order to maintain reproducibility. While the system with differential dilution and the pumping parameters shown in Fig. 3b allowed a sampling rate of only 80 samples/h, the system comprising dialysis (Fig. 3a) permitted a rate of 125 samples/h. Figure 5 shows an actual recording with the latter system.

In retrospect, an embarrassingly large number of aqueous chloride standards, serum pools and serum standard materials was analyzed before it was realized that the systematic deviation generally observed between all the aqueous standards and all the serum samples was due partly to the mixing of the sample plug with the carrier stream before dialysis and partly to the dialysis itself. As can be seen from Table 1, a deviation of ca. −15 to +30 % between all serum standards and the aqueous standards could be obtained depending on the system used, although regression analysis on the aqueous standards for each dialysis system consistently yielded regression coefficients

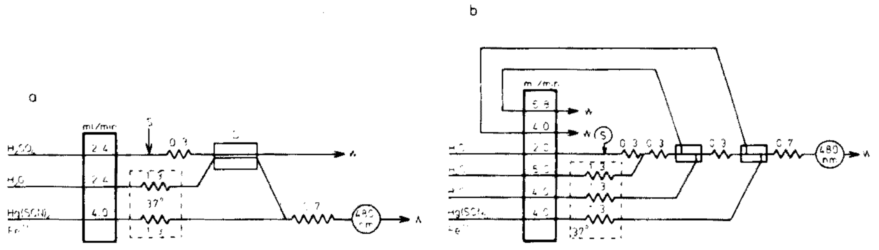
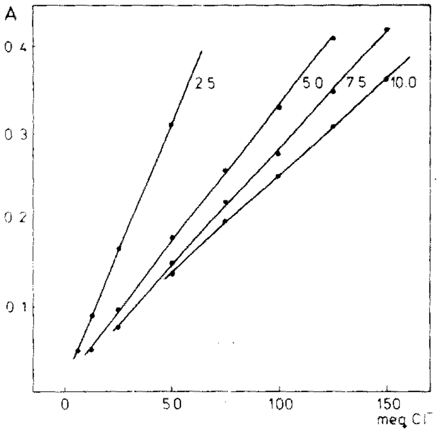


Fig. 3. Manifolds for the determination of chloride in serum using (a) dialysis (D); and (b) double dilution based on differential pumping. Both manual injection (S) as well as automated sampling by means of the sample loop (Fig. 2) were used.



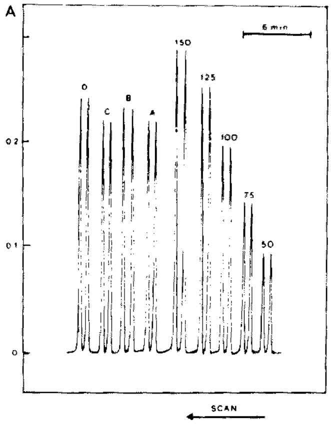


Fig. 4. The influence of the pumping rates of carrier and recipient streams (ml min^{-1}) on the peak heights of aqueous chloride standards, as obtained by injection of 200-μl samples into the manifold of Fig. 3a.

Fig. 5. Determination of chloride in serum by dialysis (Fig. 3a), after automatic injection of 60-μl samples by the sample loop of Fig. 2. The aqueous standards covered the concentration range 50—150 meq l^{-1}. The four serum samples are: A. Serum Pool; B. Technicon SMA 2; C. Moni-trol I; and D. Moni-trol II.

TABLE 1

Determination of chloride in serum samples by Flow Injection Analysis with either dialysis or differential dilution of the injected samples

Serum sample	Stated or assign. values ($\pm 2 s_r$) (meq l^{-1})	With dialysis				Without dialysis	
		Manual inj.[a] 200 μl (meq l^{-1})		Autom. inj. 60 μl (meq l^{-1})		Autom. inj. 30 μl (meq l^{-1})	
Auto-Ref	102 ± 3	84	*101*	—	—	—	—
Moni-trol I	102 ± 3	85	*102*	110	*102*	130	*102*
Moni-trol II	116 ± 4	97	*116*	122	*113*	—	—
Technicon SMA 2	103	—	—	114	*105*	134	*105*
Pool	101	85	*102*	109	*101*	126	*99*

[a] Based on aqueous standards; the italicized values are based on Moni-trol I as an internal standard of value 102 meq l^{-1}.

of 0.999 or better and standard errors of ca. 1.5 %. The corresponding values for the differential dilution system were slightly poorer, probably because of the pulsating effect of the pump, which at the extensive dilutions used implies that pulses in all conduits should be phased to obtain optimal reproducibility. It is noteworthy, however, that the serum standard samples yield values which remain in the same relation to each other. Thus, for a particular system, sample volume, acidity of donor stream and length of mixing coil, a certain systematic but reproducible deviation could be found between the chloride present in the aqueous and the serum samples, and by choosing one of the serum samples as an internal standard, values similar to those stated for the serum standards were obtained. Furthermore, it appears that the process of dialysis merely serves as a very accurate procedure of dilution, for the species of interest as well as for interfering agents, and that this process can be accomplished equally well by a simple but carefully controlled dilution of the sample.

The deviation found between the aqueous and the serum samples are said not to occur in the dialyzer unit of the AutoAnalyzer system; further comparative studies of continuous dialysis of air-segmented and non-segmented streams may thus be warranted.

Determination of phosphate

Based on the experience gained with the chloride systems, the phosphate determinations of the aqueous and the serum standard solutions were done mainly on systems without dialysis (Fig. 6a), injecting 200 μl samples. This direct measurement procedure, in which 1/5 sample aliquots obtained by differential dilution were allowed to mix with the molybdenum blue colour-forming reagents, yielded results which with one exception (Auto-Ref) showed no systematic deviation between the aqueous standards and the serum samples (Table 2); the regression coefficient of the calibration plot was 0.9996 and the standard error amounted to only 0.6 %. Furthermore, this simple manifold allowed the analysis to be performed at a rate of 130 samples/h (Fig. 7). Provided that glycerine was present in the reagent streams, a stable baseline signal was obtained, and the slope of the calibration curve achieved with the aqueous standards was not altered by any number of intermittently injected serum samples. The system involving dialysis (Fig. 6b), in which 100-μl samples were injected automatically, gave satisfactory results (Table 2), yet ostensibly

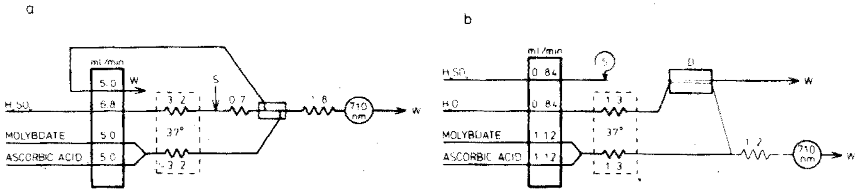


Fig. 6. Manifolds for the determination of phosphate in serum with (a) differential dilution, and (b) dialysis. Both manual and automatic sample injections were used. In (b) the thin lines denote polyethylene tube of 0.75 mm i.d., including the 1.12-m mixing coil.

TABLE 2

Determination of the inorganic phosphate content in serum samples by Flow Injection Analysis with and without dialysis of the injected samples

Serum sample	Stated or assign. values ($\pm 2\, s_r$) (mg P/100 ml)	Differential dilution manual injection 200 μl (mg P/100 ml)	With dialysis autom. injection 100 μl (mg P/100 ml)
Auto-Ref	4.5 ± 0.3	4.0	—
Moni-trol I	3.4 ± 0.2	3.5	3.4
Moni-trol II	4.6 ± 0.3	4.3	5.0
Technicon SMA 2	5.4	—	4.8
Pool	3.4	3.4	3.4

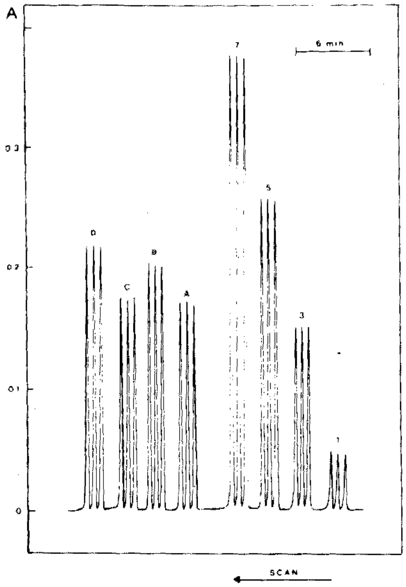


Fig. 7. Determination of phosphate in serum by differential dilution (Fig. 6a) with manual injection of 200-μl samples. The aqueous standards covered the concentration range 1—7 mg P/100 ml. The four serum samples are: A. Serum Pool; B. Auto-Ref; C. Moni-trol I; and D. Moni-trol II.

too low a value for the Technicon SMA 2 serum standard; although the regression data were adequate (regression coefficient 0.9994, standard error 0.9 %), the sampling rate was only 50 samples/h. The low sampling rate was caused by the need to increase the yield of dialysis which was done by slowing the pumping rates and so prolonging the residence time of the sample plug in the dialyzer, and increasing the dialysis path. However, even when the long dialysis unit and pumping speeds as low as 0.8—1 ml min^{-1} (Fig. 6b) were used with a measuring cell with an optical path length of 20 mm, the highest absorbance signals recorded were only of the order of 0.1 absorbance units.

DISCUSSION

Standardization has some special aspects in clinical analysis. The blood samples are complex; in addition to different chemical species, they also contain cells and particulate matter within which the analyte is distributed. Therefore, lyophilization is nearly always used to obtain a homogeneous sample, from which all particulate matter has been removed by centrifugation or filtration. Even serum samples prepared in this manner differ considerably from aqueous samples, and also often from each other in fat content, protein content, viscosity, opalescence, etc. Consequently, their analysis and comparison with aqueous standards by methods involving dialysis or other membrane processes, e.g. ion-selective electrodes, often presents problems. This has been recognized and dealt with by developing serum reference standards for instrument calibration. These standards are made from human blood serum or are reconstituted from animal materials. When used in certain instruments these materials then yield the "normal" or "recommended" values. This approach might be acceptable for a routine clinical laboratory, but problems arise if results of two or more laboratories are to be compared, particularly if different instruments are being used. This can readily be illustrated by the fact that manufacturers of serum standard materials list different "standard values" for different types of analyzer. To avoid this problem becoming apparent, some of the most recent instruments are not even calibrated by aqueous standards [10].

The limited experience with serum analysis obtained in the present work indicates that even dialysis cannot completely eliminate this systematic deviation. Although dialysis is still preferable in chloride determinations, mainly as a means of dilution, it could be avoided in the phosphate determination where high values for inorganic phosphate were not found on undialyzed serum samples. Thus it appears that the short residence time of the sample in the coil where the molybdenum blue is formed is not sufficient to allow the reaction of organically bound phosphate. Although the phosphate determinations described here were performed with 200-μl samples injected manually, equally satisfactory results could be obtained with automated loop injection of 100 μl or even smaller serum volumes. It is believed that sample dilution combined with an automated blanking, if required, might be found useful in many other clinical determinations.

Conclusion

Dialysis can be performed on serum samples without distorting the sample zones formed in the Flow Injection procedure. For the determination of chloride, a well designed dialyzer allows satisfactory sampling rates to be obtained consistent with high reproducibility. However, simple sample dilution, if compatible with the colour-forming reaction, appears to be preferable, for dialysis is unlikely to eliminate completely the systematic error frequently observed between serum samples and aqueous standards.

Semi-automated microsampling has been developed which, besides being well suited for full automation, also ensures a smooth flow pattern even during the sampling period. This in turn will allow slower reactions to be adopted for the Flow Injection technique without loss of sampling rates, as several samples could be accommodated in a longer analytical line at the same time. In this connection, it should be pointed out that the pumping rates used in this work were slower than those used in the first papers of this series. Evidence exists that the turbulent flow as defined by the Reynolds number is not required to preserve a discrete sample pattern in the unsegmented continuous flow system. The theoretical treatment and the important parameters affecting the exit age distribution curve of the injected sample zone will be given in a later part of this series. Meanwhile, the next paper will be devoted to the use of ion-selective electrodes as detectors in the Flow Injection system.

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REFERENCES

1 E. H. Hansen and J. Růžička, Danish. Pat. Appl. No. 4846/74, Sept. 1974.
2 J. Růžička and E. H. Hansen, Anal. Chim. Acta, 78 (1975) 145.
3 J. Růžička and J. W. B. Stewart, Anal. Chim. Acta, 79 (1975) 79.
4 J. W. B. Stewart, J. Růžička, H. Bergamin Filho and E. A. G. Zagatto, Anal. Chim. Acta, 81 (1976) 371.
5 J. Růžička, J. W. B. Stewart and E. A. Zagatto, Anal. Chim. Acta, 81 (1976) 387.
6 J. W. B. Stewart and J. Růžička, Anal. Chim. Acta, 82 (1976) 137.
7 H. W. Holy, Dialysis: its essential role in automated analysis in Biologie Prospective, Proc. II^{e} Colloque de Pont-A-Mousson, 1972; L'expansion Scientifique Francaise. (Ed.).
8 Technicon AutoAnalyzer II Method No. SE4-0005FD4, April 1974.
9 Technicon AutoAnalyzer II Method No. SE4-0004FH4, August 1974.
10 H. Diebler and M. Pelavin, Advances in Automated Analysis, 1972, Techn. Int. Congr. Vol. 1, Mediad Inc., 1973, p. 19.
11 B. Zak, J. Salancy, W. L. Clark, S. S. Marie and E. Baginski, Advances in Automated Analysis, 1972, Techn. Int. Congr. Vol. 1, Mediad Inc., 1973, p. 151.

Analytica Chimica Acta, 87 (1976) 365—373

REDOX-EXTRACTION CHROMATOGRAPHY. INTERACTION BETWEEN 2,5-DI-TERT-PENTYLHYDROQUINONE AND TRI-n-OCTYLPHOSPHINE OXIDE IN CYCLOHEXANE SOLUTION, AND FURTHER ANALYTICAL APPLICATIONS

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SUMMARY

Redox-extraction chromatography with 2,5-di-tert-pentylhydroquinone (DPHQ) and tri-n-octylphosphine oxide (TOPO) has been extended to a wider range of hydrochloric acid concentrations for the retention of Th, U, Np and Pu. This system behaves antagonistically with respect to tetra and hexavalent ions at some acidities. When DPHQ is oxidized to the quinone form this effect disappears; the DPQ—TOPO system shows simple redox-extraction features. These results have been used to obtain separations of Pu—Np—U on DPHQ—TOPO and DPQ—TOPO columns.

Redox-extraction chromatography is a new method for the separation of some actinide elements [1]; a solution in cyclohexane of tri-n-octylphosphine oxide and a hydroquinone is supported on a solid polymeric material. The separations of Pu—Np, Am—Np and Pu—U were obtained in 6 M HCl on the basis of the reducing and extracting properties of the stationary phase.

The main features of such columns are: (a) the possibility of transforming the reductant to the corresponding oxidized compound and vice-versa; (b) good retention of the extractant and of the redox compound on the column; (c) uniform distribution of the redox compound all along the column; (d) the possibility of achieving some separations of actinide elements at trace level without conventional redox systems.

The present work extends this technique to the retention of thorium, uranium, neptunium and plutonium on such columns over a wider range of HCl concentration, and to further applications.

EXPERIMENTAL

Equipment and reagents

A liquid scintillation spectrometer (Intertechnique model S. L. 30) was used for the β- and α-counting. Insta-Gel (Packard, U.S.A.) was used as scintillation fluid. α-Spectrometry was performed with a solid-state detector connected to an Ortec chain and a Laben 400-channel analyzer.

The chromatographic columns made of Perspex had an internal diameter of 1 cm. Microthene-710 (microporous polyethylene; 50-100 mesh; Columbia Organic Chem.) was used as the inert support in the redox-extraction columns.

2,5-Di-tert-pentylhydroquinone (DPHQ; Eastman Kodak) was employed as the redox reagent and tri-n-octylphosphine oxide (TOPO; Eastman-Kodak) as the extractant. All other reagents were analytical grade (C. Erba).

The purity of the actinide elements (^{233}U, ^{237}Np, ^{239}Pu; Amersham Radiochemical Centre) was checked by α-spectrometry. ^{234}Th (UX$_1$) was prepared by extracting the parent ^{238}U from 6 M HCl with tri-n-octylamine. ^{233}U and ^{234}Th tracers were each mixed with their natural isotopes as carriers at a concentration of 10 μg/sample.

Np(IV) was prepared by reduction; 0.05 M hydroxylammonium chloride was added to hydrochloric acid solutions of neptunium [2].

Pu(IV) was obtained by gentle evaporation of the stock nitrate solution in the presence of hydroxylamine; the residue was then dissolved in a very small volume of 1 M HNO_3 containing $NaNO_2$. This solution was finally diluted with 1 ml of HCl of the required concentration [3].

Np(VI) and Pu(VI) were prepared by adding potassium chlorate to hydrochloric acid solutions of the two elements and heating at 70 °C [2].

Preparation of redox-extraction columns

DPHQ—TOPO column. A solution in cyclohexane containing 0.1 M DPHQ and 0.1 M TOPO was prepared; 2 ml of this solution was added to 2.5 g of Microthene and the slurry was transferred to a column with ca. 40 ml of distilled water.

DPQ—TOPO column. 8 ml of 0.1 M cerium(IV) sulphate was passed through a DPHQ—TOPO column to achieve quantitative oxidation of the hydroquinone to the quinone form. The column was washed with ca. 50 ml of distilled water until free from cerium(IV). The excess of cerium(IV) was titrated iodometrically.

Actinide retention and separation experiments

Aliquots of 20,000 d.p.m. of each radionuclide were used for each retention experiment on DPHQ—TOPO and DPQ—TOPO columns.

In preliminary experiments, the test solution was prepared without standardization of the radionuclide valence state. Each column was conditioned with hydrochloric acid at the desired concentration and then loaded with 1 ml of the same hydrochloric solution containing the tracer. After washing with a further 50 ml of the hydrochloric solution, a successive elution with 40 ml of 1 M hydrofluoric acid was employed to determine the percentage of radionuclide retained on the column. For this purpose the two fractions were evaporated (the second in a Teflon beaker) and their activity was determined by α-counting.

When the retention of a single valency state of neptunium and plutonium was studied, the column washing and the successive elution were done with a hydrochloric acid solution containing the respective "holding" redox system in order to avoid disproportionation reactions or redox effects from the presence of DPHQ and DPQ in the organic phase.

The Pu—Np—U separations were achieved with HCl solutions to which redox compounds were not added. The elution diagrams were obtained by collecting 3-ml fractions of the eluate, and α-spectrometry was performed to determine any overlapping of fractions. Each column was used for one experiment only; the flow-rate was 0.25 ml min^{-1}.

Thorium liquid—liquid extraction

The TOPO and DPHQ—TOPO solutions were the same as used for column preparation. The DPQ—TOPO solution was prepared by shaking 12 ml of 0.1 N Ce(IV) sulphate with 4 ml of the DPHQ—TOPO solution to achieve quantitative oxidation of DPHQ to DPQ. The organic solution was washed with distilled water and the excess of Ce(IV) was titrated iodometrically.

The distribution coefficients of thorium were determined by stirring 3 ml of aqueous solution with 3 ml of pre-equilibrated organic solution for 3 min. The phases were separated by centrifugation and aliquots (2 ml) were taken for β-counting.

RESULTS

Retention of non-standardized solutions

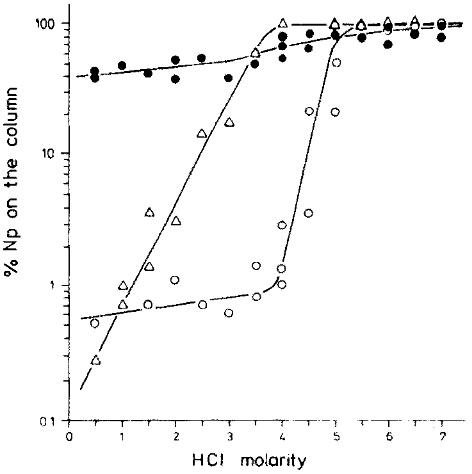
The retention of neptunium (Np(IV) + Np(V) + Np(VI)) on DPHQ—TOPO and DPQ—TOPO columns was studied as a function of the hydrochloric acid concentration and compared with the retention on TOPO columns. Figure 1 shows that the amount of neptunium retained on the TOPO column increases from 40 % to about 90 % when the acidity of the aqueous solution changes from 0.5 to 7 M hydrochloric acid. When DPHQ is present in the organic phase the retention is low in the range 0.5—4 M HCl, but increases to ca. 100 % in 5—7 M HCl. Similar behaviour is obtained with a DPQ—TOPO column, but the curve is shifted towards lower values of acidity.

Figure 2 shows that uranium is completely extracted on TOPO and DPQ—TOPO columns from 0.5 to 7 M HCl, but less than 1 % is retained on the DPHQ—TOPO column in the range 0.5—2.3 M HCl; the retention increases to ca. 100 % for 4—7 M HCl.

The behaviour of plutonium (Pu(III) + Pu(IV) + Pu(VI)), differs (Fig. 3). The retention curves present a minimum with a factor of 10 to 100 between the TOPO (DPQ—TOPO) and DPHQ—TOPO columns.

Retention of single valence states

These experiments were repeated with single valence states of neptunium and plutonium and the behaviours of Th(IV) and U(VI) were studied. The



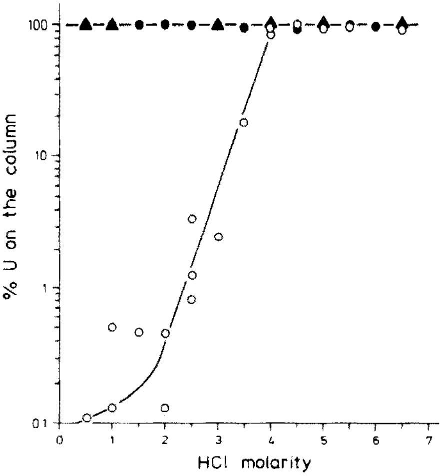


Fig. 1. % Retention of unstandardized neptunium (Np(IV) + Np(V) + Np(VI)) on TOPO, DPHQ—TOPO, and DPQ—TOPO columns as a function of the hydrochloric acid concentration. ● 0.1 M TOPO. ○ 0.1 M TOPO—0.1 M DPHQ. △ 0.1 M TOPO—0.1 M DPQ.

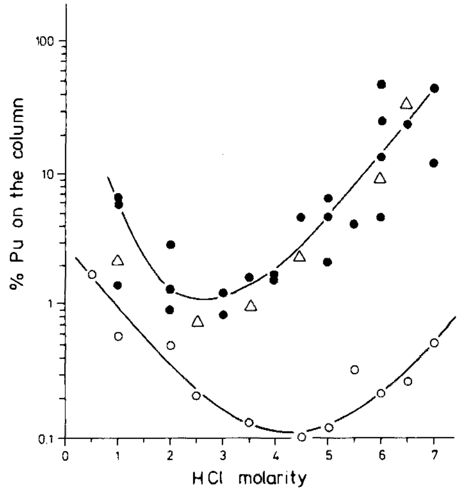
Fig. 2. % Retention of uranium(VI) on TOPO, DPHQ—TOPO, and DPQ—TOPO columns as a function of the hydrochloric acid concentration. Symbols as in Fig. 1.

results are reported in Table 1; the tetra- and hexavalent ions behave in the same way on TOPO and DPQ—TOPO columns, but are retained less on the DPHQ—TOPO column. The liquid-liquid extraction data of thorium(IV) (Fig. 4) agree well with these results. The distribution coefficients with the DPHQ—TOPO solution are lower than those obtained with TOPO [4] and DPQ—TOPO solutions. When the concentration of DPHQ was increased from 0 to 0.1 M, the distribution coefficient of thorium between 4 M HCl and 0.1 M TOPO in cyclohexane fell from 51.2 to 0.061.

Separations

The separation program was studied for each radionuclide independently to obtain the data reported in Tables 2 and 3; the amount of each element in the single fractions collected from the columns was compared with that obtained with TOPO columns. The values indicate a good separation of each radionuclide; changing the experimental parameters may give an improvement.

As a result, two separations have been obtained. Plutonium, neptunium, and uranium have been separated on a DPHQ—TOPO column by eluting with 6.5, 4, and 0.5 M HCl successively. The elution diagram is shown in Fig. 5. The same elements have been separated on a DPQ—TOPO column by eluting plutonium and neptunium with 4 and 0.5 M HCl respectively and uranium with 1 M HF (Fig. 6).



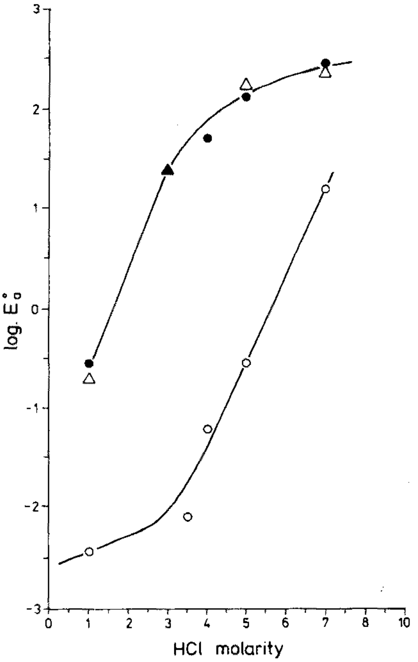


Fig. 3. % Retention of unstandardized plutonium (Pu(III) + Pu(IV) + Pu(VI)) on TOPO, DPHQ—TOPO, and DPQ—TOPO columns as a function of the hydrochloric acid concentration. Symbols as in Fig. 1.

Fig. 4. Liquid—liquid extraction of thorium(IV) by TOPO, DPHQ—TOPO, and DPQ—TOPO in cyclohexane. Behaviour of the distribution coefficients as a function of the hydrochloric acid concentration. Symbols as in Fig. 1.

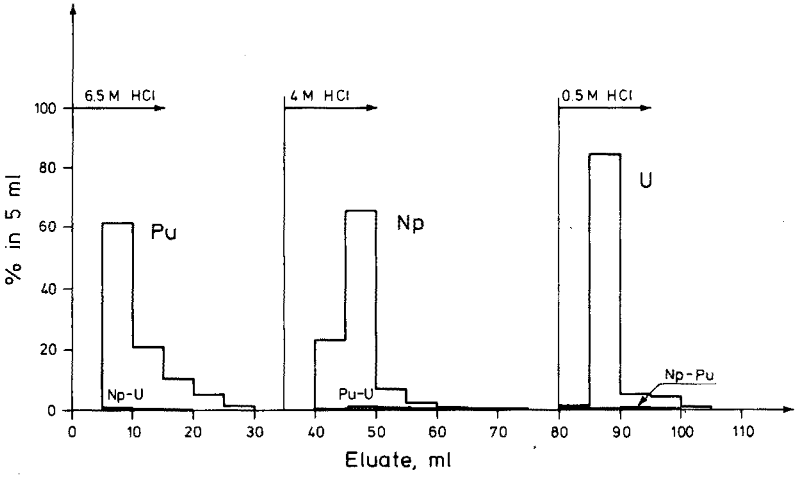


Fig. 5. Plutonium—neptunium—uranium separation on a DPHQ—TOPO column.

TABLE 1

% Retention of single valence states of some actinide elements on a TOPO and redox-extraction columns

HCl (M)	TOPO column					
	Th(IV)	U(VI)	Np(IV)	Np(VI)	Pu(IV)	Pu(VI)
0.5	0.58	99.9	23.0	—	—	—
1.0	—	99.3	—	24.7	26.0	96.8
1.5	0.25	99.4	28.0	—	—	—
2.0	—	99.2	—	—	97.2	97.9
2.5	3.03	99.7	93.7	—	—	—
3.0	46.2	99.5	—	98.5	—	—
3.5	98.7	98.7	99.8	—	—	—
4.0	94.9	99.9	—	97.5	99.2	97.7
4.5	99.3	95.9	—	—	—	—
5.0	—	99.2	94.5	—	—	—
5.5	99.5	99.7	—	—	—	—
6.0	—	99.1	93.6	99.0	99.0	97.8
6.5	98.3	99.6	—	—	—	—

HCl (M)	TOPO—DPHQ column			TOPO—DPQ column				
	Th(IV)	U(VI)	Np(IV)	Th(IV)	U(VI)	Np(VI)	Pu(IV)	Pu(VI)
0.5	0.51	0.11	0.37	0.71	99.6	25.0	—	—
1.0	—	0.31[a]	—	—	98.3	15.5	78.1	10.8
1.5	0.30	0.45	0.97	0.52	—	—	—	—
2.0	—	0.28[a]	—	—	—	50.0	88.5	97.5
2.5	1.20	1.27[a]	1.73	4.80	—	—	—	—
3.0	—	2.49	—	39.2	99.9	96.6	—	—
3.5	1.60	17.9	—	97.9	—	—	—	—
4.0	—	91.6[a]	2.70	98.5	99.8	99.2	98.2	98.2
4.5	1.10	98.7	—	99.4	—	—	—	—
5.0	—	96.5	99.9	—	99.7	—	—	—
5.5	1.30	99.6	—	99.8	—	—	—	—
6.0	—	99.8	99.8	—	—	99.2	96.4	98.2
6.5	10.4	99.0	—	99.6	99.8	—	—	—

[a] Mean value of 2 or 3 determinations (see Fig. 2).

DISCUSSION

Previous retention experiments [1] with neptunium and plutonium on a DPHQ—TOPO column have been extended to a wider range of hydrochloric acid concentrations and the results have been compared with those obtained with a TOPO column. Neptunium (Np(IV) + Np(V) + Np(VI)) (Fig. 1), is completely retained on the DPHQ—TOPO column when the hydrochloric acid concentration is higher than 5 M. This result, expected from previous

TABLE 2

Percentage distribution of uranium, neptunium and plutonium in fractions collected from TOPO and DPHQ—TOPO columns

Radio-nuclide	TOPO column			DPHQ—TOPO column		
	6.5 M HCl 35 ml	4 M HCl 45 ml	0.5 M HCl 30 ml	6.5 M HCl 35 ml	4 M HCl 45 ml	0.5 M HCl 30 ml
Pu	72.3	25.6	2.1	99.2	0.6	0.2
Np	13.0	0.7	86.3	0.1	97.8	2.1
U	0.1	0.1	0.9	0.9	3.2	95.9

data [1], can be interpreted on the basis of complete reduction of neptunium to Np(IV), which is ca. 100 % extracted by the TOPO. The poor retention of neptunium at low acidities was inconsistent with this interpretation; Np(IV) was therefore passed through DPHQ—TOPO and TOPO columns and Table 1 shows that it is not retained on a DPHQ—TOPO column in 0.5—4 M hydrochloric acid although its retention on a TOPO column is much higher. Thorium(IV), having a single valency state, shows a similar effect, as does uranium(VI) (Fig. 2); the hexavalent state cannot be reduced on such columns. The decreased extraction of the tetra- and hexavalent ions at low acidity with the DPHQ—TOPO column might raise doubts about the reduction of neptunium to Np(IV) under these conditions (Fig. 1).

The case of plutonium (Pu(III) + Pu(IV) + Pu(VI)) seems to be simpler (Fig. 3). Its retention on a TOPO column is very low in a wide range of acid concentrations because of the large fraction of Pu(III) present in the feed solution, and it decreases still more when a DPHQ—TOPO column is used because of the further reduction of Pu(IV) and Pu(VI) to Pu(III) [5].

The possibility of obtaining redox reactions on DPQ—TOPO columns has been examined. Figure 1 shows that a low retention is obtained for neptunium at low acidities. However a negative effect of DPQ on the

TABLE 3

Percentage distribution of uranium, neptunium and plutonium in fractions collected from TOPO and DPQ—TOPO columns

Radio-nuclide	TOPO column			DPQ—TOPO column		
	4 M HCl 45 ml	0.5 M HCl 45 ml	1 M HF 30 ml	4 M HCl 45 ml	0.5 M HCl 45 ml	1 M HF 30 ml
Pu	97.3	2.2	0.5	98.2	1.8	0.0
Np	42.3	56.3	1.4	6.6	93.4	0.1
U	0.7	0.6	98.7	0.2	0.2	99.6

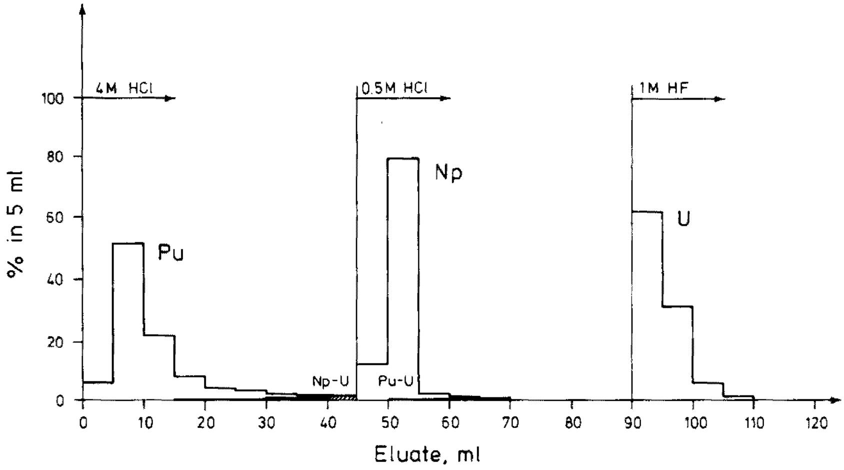


Fig. 6. Plutonium—neptunium—uranium separation on a DPQ—TOPO column.

extraction of Np(IV) and Np(VI) does not seem possible; the results in Table 1 show that tetravalent and hexavalent ions have the same retention on DPQ—TOPO and TOPO columns. An oxidation of Np(IV) to Np(V) by DPQ may therefore take place when the concentration of hydrochloric acid is lower than 4M. When the concentration of hydrochloric acid exceeds 4 M, Np(VI) may be formed preferentially with subsequent extraction of ca. 100 %. The results obtained (Fig. 4) with three different extracting solutions (TOPO; DPQ—TOPO; DPHQ—TOPO) confirmed for thorium the negative effect of DPHQ and the absence of any effect of DPQ on the TOPO extraction features.

The behaviour of tetravalent and hexavalent ions on the DPHQ—TOPO column suggests that the extractant and the reductant are associated in the organic phase in such a way that the extraction capability of TOPO is strongly hindered. In fact, the liquid—liquid extraction of thorium(IV) decreased rapidly after the addition of DPHQ. Similar effects were observed for extracting mixtures which behave as anti-synergic or antagonistic systems [6]. This is also supported by the solubility data for DPHQ at room temperature: the molar solubility of DPHQ, which is about 10^{-2} in cyclohexane, increases to 0.13 in a solution (0.1 M) of TOPO in cyclohexane. The DPHQ—TOPO system therefore does not operate as a single redox-extraction system at some values of acidity because the two components are associated in the organic phase. In contrast, the DPQ—TOPO system does not show a similar effect and its behaviour should be interpreted in terms of a simple redox-extraction mechanism.

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REFERENCES

1 A. Delle Site and C. Testa, Anal. Chim. Acta, 72 (1974) 155.
2 E. Akatsu, JAERI, 1099 (1965).
3 S. C. Foti and E. C. Freiling, Talanta, 11 (1964) 385.
4 W. J. Ross and J. C. White, ORNL-2627 (1958)
5 C. Coleman and B. S. Weaver, U.S.A. Patent 3, 580 (1971) 705.
6 Y. Marcus and A. S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, Wiley-Interscience, 1969, p. 847.

Analytica Chimica Acta, 87 (1976) 375–386

SOLVENT EFFECTS IN GEL CHROMATOGRAPHY: THE RELATIONSHIP BETWEEN THE DISTRIBUTION COEFFICIENTS OF METAL ACETYLACETONATES AND SOLUBILITY PARAMETERS OF SOLVENTS

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SUMMARY

Distribution coefficients of metal acetylacetonates such as $Al(acac)_3$, $Cr(acac)_3$ and $Co(acac)_3$ etc., and n-alkanes in porous polystyrene gel chromatography with ten organic solvents as eluants were estimated and compared with those obtained by the batch method in two solvent systems. Solubility parameters of the metal acetylacetonates were determined. There is a relationship between the distribution coefficients and solubility parameters of solutes and solvents. Two factors (steric exclusion and partition) play important rôles in each solvent for the separation mechanisms of the present systems. The latter factor was estimated successfully from a regular solutions approximation.

The interactions between metal chelate cations and solvents have been studied by conductimetric [1] and solubility [2] measurements, and the solvation by alcohols of a neutral metal chelate of tris(acetylacetonato)-cobalt(III) has been reported [3]. The interactions between metal chelate solutes and solvents are of fundamental importance in studies of the mechanisms of extractions and also of liquid chromatography. It has been suggested [4] that mutual interactions among a solute, a solvent and the gel are important for the separation of neutral complexes such as metal acetylacetonates, and a solubility parameter seems to be useful in such systems.

In the present paper, distribution coefficients of metal acetylacetonates and n-alkanes between organic solvents and polystyrene gel were determined by the column system. In some cases, these coefficients are compared with those obtained by the batch method. Solubility parameters of tris(acetylacetonato)aluminum(III), chromium(III) and cobalt(III) are estimated from solubilities in benzene and carbon tetrachloride, and the elution volumes of acetylacetonates in different solvent systems are interpreted by regular solutions treatment in terms of the solubility parameters of solvents, gel and metal acetylacetonates.

To explain the separation mechanisms of gel chromatography with porous polymer gels, theories such as steric exclusion [5], restricted diffusion [6], partition [7] and thermodynamic equilibrium [8] have been proposed; more than two factors must be taken into consideration. Huber et al. [9] have reported the separation of metal acetylacetonates by liquid—liquid chromatography with ternary solvent systems, and Suzuki and co-workers [10] have studied polyvinyl acetate gel—organic solvent systems.

EXPERIMENTAL

Reagents and instruments

Metal (Al, Cr, Co, Fe, Cu, Ni) acetylacetonates (Dojin Co.) were recrystallized from appropriate solvents; purities were checked by carbon and hydrogen analyses (all the results were accurate within the normally accepted limits) and by electronic spectra. Monodisperse polystyrene-4000 (M_w/M_n less than 1.1) was used to measure void volumes. Reagent-grade n-alkanes were used without further purification (Wako Pure Chem. Ltd.). Reagent-grade solvents were distilled before each measurement from a vacuum-jacketed column (length 4 ft.) packed with glass beads. Concentrations of sample solutions were $5 \cdot 10^{-4}$—$1 \cdot 10^{-1}$ M for metal acetylacetonates and n-alkanes, and 0.05—0.5 % for polystyrene.

A Toyo Soda High Speed Liquid Chromatograph Model HLC-801 with two columns (each 610 mm × 6 mm), and a Shimadzu GPC-1A with one column (1220 mm × 8 mm), were used. A recording differential refractometer was used as a detector. The styrene-divinylbenzene copolymer gels (porous polystyrene gel) used were Toyo Soda TSK G-1000 H (10^1 Å) or Shimadzu SG-1—SG-5. The fractionation ranges were: SG-1, 10^1—10^2; SG-2, 10^2—$5 \cdot 10^4$; SG-3, $5 \cdot 10^4$—10^5; SG-4, 10^5—$5 \cdot 10^5$; SG-5, $5 \cdot 10^5$—10^6.

Standard conditions for measurements were as follows: flow rate, 1 ml min^{-1}; column temperature and room temperature, ca. 25 °C; sample injection, 60 μl (HLC-801), 0.5 ml (GPC-1A). Absorption spectra of $Al(AA)_3$, $Cr(AA)_3$ and $Co(AA)_3$ before and after each elution showed that they were stable in these systems.

Batch method (equilibrium method)

Dry gel (7—9 g, SG-1) and 20 ml of a sample solution were placed in glass stoppered bottles and equilibrated by stirring for 10—24 h in a water bath at 25 ± 0.05 °C. After equilibrium had been attained, the supernatant solutions were taken up through glass filters and the concentration of metal acetylacetonate was determined by spectrophotometry. Concentrations of polystyrene and n-alkanes were obtained by gel chromatography.

Solubility measurements of metal acetylacetonates

Solvent (100 ml) was stirred with excess of crystals in a water bath at 25.00 ± 0.005 °C for 2—6 h. The concentrations were checked every hour by withdrawing aliquots through glass filters. Equilibrium was attained within 3 or

4 h. The concentrations of metal acetylacetonates were determined by spectrophotometry.

RESULTS

Conditions for column systems

The dependence of elution volume on flow rate was examined in the range 0.5—4 ml min^{-1} and was negligible for flow rates smaller than 2.0 ml min^{-1}. The elution volumes of tris complexes of Cr and Co are not concentration-dependent; complexes of Al are slightly dependent and the tris complexes of Mn and Fe as well as the bis complexes of Cu and Ni exhibit large dependences. The relatively labile characters of the complexes or their strong interactions with the gel phase because of the geometric factor of the bis complexes may be responsible. Concentration dependences of these complexes are larger when eluted by chloroalkanes or tetrahydrofuran than when eluted by aromatic solvents. Some typical examples are given in Fig. 1.

The effect of temperature on the elution volumes follows similar trends as shown in Fig. 2; the elution volumes of tris complexes of Cr, Co and Al are constant, but those of tris complexes of Fe and Mn, and those of bis complexes of Cu and Ni, increase slightly with increasing column temperature.

Distribution coefficients

The values of K_{av} given in Tables 1 and 2, were calculated from

$$V_e = V_o + K_{av} (V_t - V_o) \qquad (1)$$

where V_e, V_o and V_t are the elution volume, void volume and total column volume, respectively. For the calculation of K_{av}, the elution volume of

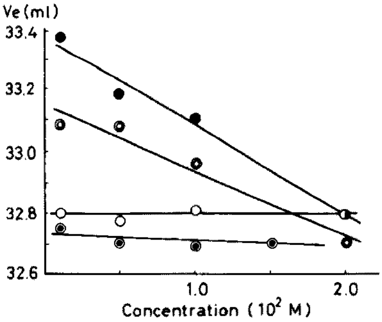


Fig. 1. Concentration dependences of elution volumes. Chloroform as eluant. Solutes —○— Cr(AA)$_3$; —◉— Al(AA)$_3$; —●— Fe(AA)$_3$; —◎— Cu(AA)$_2$.

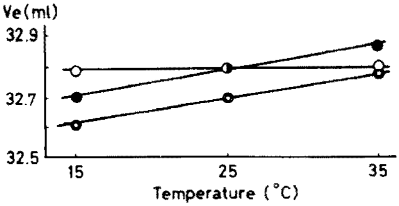


Fig. 2. Temperature dependences of elution volumes. Chloroform as eluant. Solutes: —○— Cr(AA)$_3$; —●— Fe(AA)$_3$; —◎— Cu(AA)$_2$. Concentration of sample solutions 2 · 10^{-2} M.

TABLE 1

K_{av} in various solvents for polystyrene gel TSK G-1000 H

No.	Solvent	n-Docosane (410)	n-Hexadecane (294)	n-Decane (197)	n-Pentane (116)	$Al(AA)_3$ (271)	$Cr(AA)_3$ (267)	$Co(AA)_3$ (261)
1	Chlorobenzene	0.14	0.22	0.36	0.57	0.18	0.19	0.20
2	Benzene	0.17	0.25	0.40	0.60	0.31	0.32	0.34
3	Toluene	0.15	0.23	0.38	0.59	0.41	0.46	0.51
4	*p*-Xylene	0.16	0.26	0.40	0.62	0.59	0.64	0.74
5	Dichloroethane	0.13	0.22	0.36	0.58	0.10	0.12	0.12
6	Dichloromethane	0.14	0.22	0.37	0.59	0.13	0.14	0.14
7	Chloroform	0.15	0.24	0.38	0.59	0.21	0.21	0.22
8	Carbon tetrachloride	0.13	0.21	0.35	0.56	0.48	0.57	0.69
9	Tetrahydrofuran	0.095	0.20	0.29	0.47	0.26	0.29	0.32

polystyrene-4000, which is excluded from the gel phase, is used as V_o. Distribution coefficients of metal acetylacetonates and n-alkanes by the batch method [11] were obtained from

$$C_i V_i = C_e\ (V_i - wV_s) + C_g\, \beta\, V_g \tag{2}$$

where C_i is the concentration of a solute in the supernatant solution at equilibrium, C_e is the concentration of a solute in the gel phase at equilibrium ($C_g = KC_e$), V_i is the initial volume of solution, V_s is the solvent regain of 1.0 g of dry gel, V_g is the volume of the swollen gel phase per 1.0 g of dry gel, w is the weight of dry gel and β is the fraction of the gel phase available to a solute. Abbreviating $K\beta V_g$ as α, eqn. (2) gives

$$\alpha = (V_i/w)(C_i/C_e - 1) + V_s \tag{3}$$

where V_i, C_i and C_e are known; V_s can be obtained from measurements on polystyrene which is excluded from the gel phase (α assumed to be zero). Then values of α for other compounds can be obtained by measuring values of C_e. Values of V_s for benzene, xylene, chloroform and carbon tetrachloride are given in Table 3; values of α for metal acetylacetonates and n-alkanes in benzene

TABLE 2

K_{av} of various complexes ($2 \cdot 10^{-2}$ M) in chloroform and tetrahydrofuran

	$CHCl_3$	Tetrahydrofuran		$CHCl_3$	Tetrahydrofuran
$Fe(AA)_3$	0.21	0.27	$Cu(AA)_2$	0.21	0.20
$Mn(AA)_3$	0.22	0.33	$Zn(AA)_2$	0.26	0.22
$Ni(AA)_2$	0.04	0.18			

TABLE 3

Values of V_s for the gel (25 °C)

Solvent	W(g)	C_i(% wt)	C_e(% wt)	V_s[a] (ml g^{-1} of dry gel)
Chloroform	9.1018	0.1813	0.2516	0.614
	8.9843	0.2035	0.2818	0.619
Carbon tetra-	9.0011	0.1879	0.2477	0.536
chloride	9.0178	0.1910	0.2524	0.540
Benzene	8.8270	0.1956	0.2697	0.623
	9.0100	0.1956	0.2734	0.632
p-Xylene	9.0004	0.1975	0.2653	0.568
	8.9799	0.1975	0.2608	0.540

[a] Calculated from eqn. (2) for $\alpha = 0$.

and in xylene are given in Table 4. Values of α are plotted against molar volumes in Fig. 3(a). For comparison, the values for K_{av} in benzene and in xylene are shown in Fig. 3(b).

Figures 3(a) and (b) exhibit very similar trends for the batch and column systems, indicating that the different behaviour of the n-alkanes and metal acetylacetonates in these systems does not arise from non-equilibrium or kinetic effects. The plots of metal acetylacetonates in Fig. 3 lie on different lines from those of n-alkanes; the deviations are much larger in xylene than in benzene. Any factor other than steric exclusion therefore seems to be more important for the separation mechanism of metal acetylacetonates; if steric exclusion is the dominant factor, C_i should always be smaller than C_e, as seen in the benzene system. The values of C_e for $Cr(AA)_3$ and $Co(AA)_3$ are smaller than that of C_i in xylene (Table 4), indicating that interaction with the gel phase becomes important.

TABLE 4

Values of α for n-alkanes and metal acetylacetonates at 25 °C in benzene and in xylene

	Benzene				Xylene			
	W	C_i^a	C_e^a	α^b	W	C_i^a	C_e^a	α^b
n-Docosane	7.0023	1.061	1.28	0.142	7.1086	3.92	4.65	0.108
n-Hexadecane	7.0934	3.01	3.50	0.232	6.8165	5.05	5.78	0.183
n-Decane	6.9267	2.25	2.47	0.371	6.9354	6.99	7.60	0.322
$Al(AA)_3$	6.2859	1.00	1.12	0.296	6.9889	1.06	1.15	0.322
$Cr(AA)_3$	7.3095	0.991	1.11	0.340	6.9901	1.00	0.968	0.650
$Co(AA)_3$	9.2782	1.00	1.14	0.371	6.9892	0.983	0.853	0.992

[a] 10^2 M.

[b] Calculated from eqn. (2), with values of V_s given in Table 3.

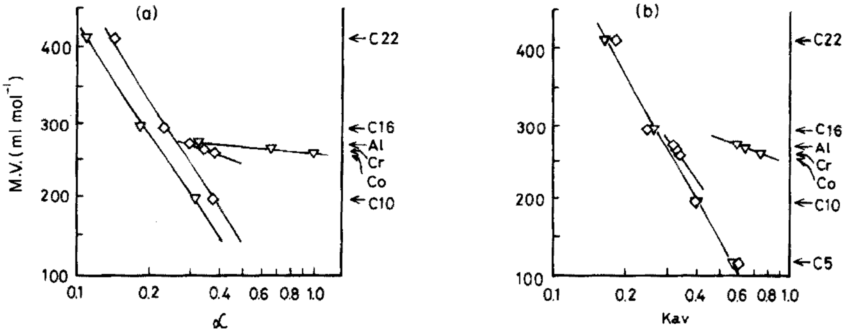


Fig. 3. Relations between molar volumes and distribution coefficients in benzene and in *p*-xylene.(a) Molar volumes vs. α. (b) Molar volumes vs. K_{av}. Eluants; —◇— benzene; —▽—*p*-xylene. Solutes: n-docosane (C_{22}); n-hexadecane (C_{16}); n-decane (C_{10}); n-pentane (C_5); $Al(AA)_3$ (Al); $Cr(AA)_3$ (Cr); $Co(AA)_3$ (Co).

Solubility parameters of the metal acetylacetonates

Molar volumes and solubility parameters of metal acetylacetonates have been presented by Irving [12]. Partial molal volumes calculated here from the densities of solutions are in good agreement with the published [12] values (in every solvent, $Al(AA)_3$, 271 ± 2; $Cr(AA)_3$, 267 ± 2; $Co(AA)_3$, 261 ± 2 ml mol^{-1}). Solubility parameters of these chelates were estimated from solubilities determined in benzene and in carbon tetrachloride (Table 5) from

$$\ln a_i = \ln X_{i(s)} + \frac{V_i}{RT}\varphi_s^2(\delta_s - \delta_i)^2 \qquad (4)$$

where a_i is the activity of a pure liquid solute at temperature T, $X_{i(s)}$ is the solubility (mole fraction) in a solvent (s), V_i is the molar volume of the solute, φ_s is the volume fraction of the solvent (s), and δ_s and δ_i are solubility parameters of the solvent (s) and solute (i), respectively.

For metal acetylacetonates, a_i is not known. To obtain δ_i, it is necessary to measure solubilities in more than two solvents. By this method, the solubility parameters of $Al(AA)_3$, $Cr(AA)_3$ and $Co(AA)_3$ are 10.2, 10.4 and 10.7, respectively (literature values [9] 10.03, 9.67 and 10.12 for $Al(AA)_3$, $Cr(AA)_3$ and $Co(AA)_3$, respectively, in chloroform, and 9.66 and 9.72 for $Cr(AA)_3$ and $Co(AA)_3$ respectively, in benzene). The molar electron

TABLE 5

Solubilities of metal acetylacetonates (Mole fraction scale 10^2 X, 25.00 ± 0.01 °C)

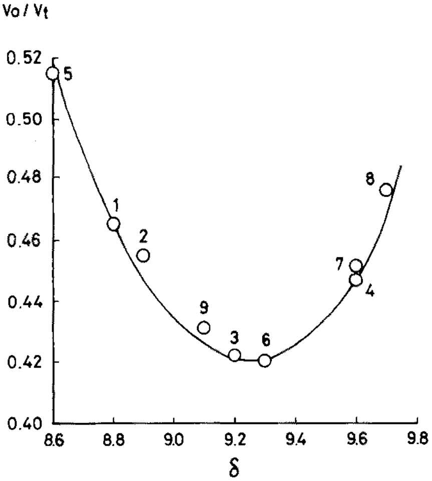
Solvent	$Al(AA)_3$	$Cr(AA)_3$	$Co(AA)_3$
Benzene	8.60 ± 0.04	6.85 ± 0.02	3.25 ± 0.04
Carbon tetrachloride	4.60 ± 0.11	3.03 ± 0.04	1.25 ± 0.05

polarizations are 91.1, 95.3 and 99.4 cm^3 for Al(AA)$_3$, Cr(AA)$_3$ and Co(AA)$_3$, respectively [13]; this may cause the difference in the solubility parameters for these homomorphic chelates. Values of V_o/V_t in various solvents are plotted against the solubility parameters of solvents in Fig. 4; the values of V_o/V_t differ in each solvent and are a minimum when the solubility parameter is 9.24. The variation of V_o/V_t is considered to correspond to a change in the degree of swelling of the gel in each solvent. The solubility parameter of the gel is taken as 9.2, the value for the solvent in which it swells to the greatest extent.

Estimation of partition coefficients

In previous papers, the changes in elution volumes of metal acetylacetonates in different solvent systems were related to the solubility parameters of solvents i.e., the elution volumes of metal acetylacetonates increased with decreasing solubility parameters of solvents. To explain a distribution coefficient larger than unity, Heitz [14] considered K_{av} to consist of two factors: (a) the volume fraction of the gel phase available for each solute, and (b) the partition coefficient of a solute between the gel phase and the solvent phase. The latter factor (K) is calculated from eqn. (5), assuming that interactions of solutes with solvents and gel phases can be treated by the theory of regular solutions [15]

$$\ln K = \ln \frac{C_g}{C_s} = \frac{V_x}{RT}(\delta_s - \delta_x)^2 - (\delta'_g - \delta_x)^2 + RT\left(\frac{1}{V_g} - \frac{1}{V_s}\right) \qquad (5)$$



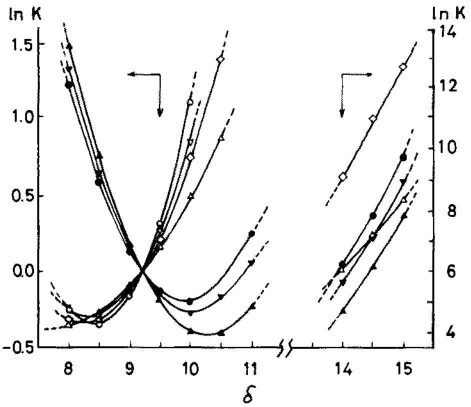


Fig. 4. Plots of V_o/V_t against solubility parameters of solvents. An elution volume of polystyrene is taken as V_o. The numbering system for solvents follows Table 1.

Fig. 5. Diagrams for changes of K with solubility parameters of solvents. Solutes: —○— n-docosane; —▽— n-hexadecane; —◇— n-decane; —△— n-pentane; —●— Al(AA)$_3$; —▼— Cr(AA)$_3$; —▲— Co(AA)$_3$.

where C_s and C_g are the concentrations in the solvent and gel phase, respectively, V and δ denote a molar volume and a solubility parameter, respectively, and subscripts x, s and g indicate solute, solvent and gel, respectively. In calculating K, the last term of eqn. (5) is assumed to be negligible and the effective solubility parameters of the gel phase (δ'_g) in each solvent system are estimated from

$$\delta'_g = \varphi_g\delta_g + \varphi_s\delta_s \tag{6}$$

where φ_g and φ_s represent volume fractions of the gel and the solvent in the gel phase. The highly cross-linked polystyrene gel is known to swell only slightly; the values of V_s given in Table 3 show that the degree of swelling does not change greatly in each solvent. The density of the gel is estimated as 1.12—1.15 by suspending the gel in solvents of different densities. So in the following calculations, fixed values of 0.6 and 0.4 are used for φ_g and φ_s, respectively, in every solvent. If δ_g is known, δ'_g can be estimated from eqn. (6). Values of ln K were calculated and illustrated in Fig. 5, where ln $K > 0$ means that a solute has greater affinity for the gel phase and elutes with a larger elution volume.

DISCUSSION

In the present systems, n-alkanes elute in the sequence C_{22}, C_{16}, C_{10} and C_5 in all solvents. Since differences in the values of K for these solutes are not large, but large differences in their molar volumes do occur, the steric effects are the dominant factor in the separation mechanisms of n-alkanes. Three metal acetylacetonates, $Al(AA)_3$, $Cr(AA)_3$ and $Co(AA)_3$, are also eluted in decreasing order of their molar volumes. But the elution volumes of these chelates become small and nearly equal when eluted with solvents whose solubility parameters are between 9.3 and 9.7. Figure 3 shows that for these chelates K is smaller than unity in these solvents, and they should be eluted with small elution volumes by the partition effect, in contrast to the case where steric exclusion acts as the only factor for the separation. Furthermore, the values of K increase in the sequence of $Co(AA)_3$, $Cr(AA)_3$ and $Al(AA)_3$; this is the reverse of the sequence expected from steric exclusion. Therefore as the differences in the molar volumes of these solutes are not so large, the two effects (partition and steric exclusion) oppose each other and the elution volumes are nearly equal. For solutes with the same molar volumes (V) but different solubility parameters (δ_1 and δ_2), eqn. (7) represents the relative change in the elution volumes in various solvents.

$$\Delta \ln K_{1,2} = \ln K_1 - \ln K_2 = \frac{V}{RT}\varphi_g(\delta_s - \delta_g)(\delta_2 - \delta_1) \tag{7}$$

$\Delta \ln K_{1,2}$ should increase with increasing φ_g and $(\delta_s - \delta_g)$. Solvents such as xylene (less swelling) are better as they increase both these terms, and highly cross-linked gels are preferable even where steric exclusion is not the only factor involved in the separation. This is shown in Fig. 6, where the

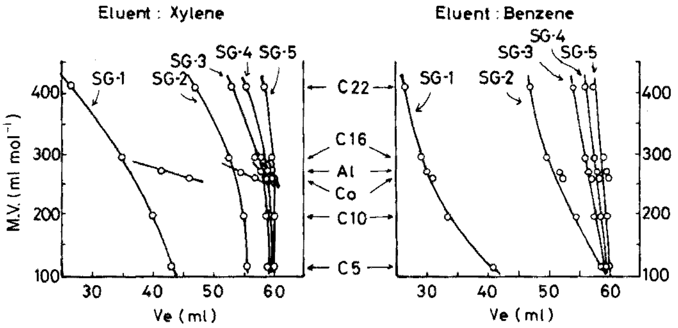
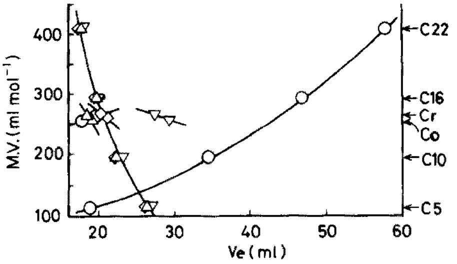


Fig. 6. Effects of pore size on elutions of n-alkanes and metal acetylacetonates. Fractionation ranges of each gel are given in Experimental. Symbols correspond to those in Fig. 3.

results of elution with gels of different pore sizes are given for two typical solvent systems. With benzene, size seems to play a dominant factor but the partition effect becomes more important in xylene. This equation also shows that the elution volume sequence will be reversed according to the sign of $(\delta_s - \delta_g)$ by changing a solvent.

Figure 5 shows that when a solvent with a large solubility parameter is used as an eluant, K becomes very large, and elution volumes would be expected to increase in the order Co(AA)$_3$ < Cr(AA)$_3$ $\approx$ C_5 < Al(AA)$_3$ < C_{10} < C_{16} < C_{22}. This is the reverse order to that observed in xylene. The results of elution with methanol (δ = 14.5) given in Fig. 7 show good agreement with the expectation that the partition effect is more pronounced than in the benzene system, where steric exclusion seems to be the dominant factor. For the separation of solutes of similar size, this solvent system is very effective, though it is slower than solvent systems where separation is by steric exclusion. If the contribution of interactions among solutes,



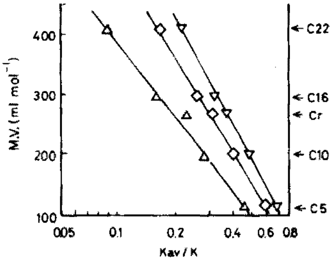


Fig. 7. Elution volumes of n-alkanes and metal acetylacetonates in four typical solvent systems. Eluants: —△— chlorobenzene; —◇— benzene; —▽— *p*-xylene; —○— methanol. Symbols correspond to those in Fig. 3.

Fig. 8. Relations between molar volumes and K_{av}/K in three typical cases. Eluants: —△— chlorobenzene; —◇— benzene; —▽— *p*-xylene. Symbols correspond to those in Fig. 3.

solvents and gel to the separation mechanisms are estimated correctly by K, then K_{av}/K should represent the distribution coefficient which is governed only by the steric exclusion effect. Therefore, when values of K_{av}/K are plotted against molar volumes, the values for metal acetylacetonates should fall on the calibration curves for n-alkanes in every solvent, as is shown in Fig. 8. Effective volumes corresponding to the value of K_{av}/K of $M(AA)_3$ were found from the calibration curves of n-alkanes to converge to 220—280 ml in all the solvents. In contrast, effective volumes obtained from K_{av} vs. molar volume plots (Fig. 3(b)) diverge between 80 and 450 ml [4] and increase with the solubility parameters of solvents.

Recently, Saitoh and Suzuki studied solvent effects in polyvinyl acetate gel—organic solvent systems [16] by means of the modified Ogston—Laurent Model [5(b)]

$$\ln K_{av} = \ln \beta' - \pi L\,(R + r_s)^2 \tag{8}$$

where L is the concentration of polymer rods in the solution (cm ml^{-1}), R is the radius of the polymer rod, r_s is the radius of a spherical solute, and R and r_s are considered to be constant in every solvent. In order to correct for the fraction of the gel phase which is not available for a solute, β' was introduced and was found to be nearly constant in every solvent by plotting $\ln K_{av}$ against $\ln K_{av}$ of a standard solute ($K_{av,o}$). The slope of the plots corresponds to $(R + r_s)^2/(R + r_{so})^2$, which is abbreviated to $(R_s/R_{so})^2$, and an interaction parameter α_{so} ($= \pi\, LR_{so}{}^2$) is obtained from

$$-\ln K_{av} = -\ln \beta' + \alpha_{so}(R_s/R_{so})^2 \tag{9}$$

In their system [16], α_{so} decreased with increasing solubility parameters of solvents. For comparison with the present systems, the same parameters were obtained; $(R_s/R_{so})^2$ was found to be 2.08, 1.53 and 0.51 for n-docosane, n-hexadecane and n-pentane, respectively (Fig. 9(a)), with n-decane taken as a standard material. These values are nearly constant for different solvents, except tetrahydrofuran. The value of β' is almost negligible for the present systems (0.91—1.04). Values of α_{so} are plotted against solubility parameters of solvents in Fig. 10; in aromatic hydrocarbons and chloroalkanes values of α_{so} fall on two distinct curves which go through a minimum at a solubility parameter of about 9.2. As α_{so} is proportional to L, it should have a minimum value in the most swelling solvent. This result is also consistent with those shown in Fig. 4. But as all the points for chloroalkanes and aromatic hydrocarbons are found to lie on one curve in Fig. 4, the difference seen in Fig. 10 for these two groups of solvents may come from differences in the interactions of solutes with solvents or the gel rather than differences in the swelling of the gel in these two groups of solvents. The effect of the interaction of solutes with solvents and gel is more important for metal acetylacetonates than for alkanes, as seen in Fig. 9(a), where it is difficult to find any correlation in the K_{av} values of metal acetylacetonates. If K_{av}/K is used instead of K_{av} in these plots (Fig. 9b),

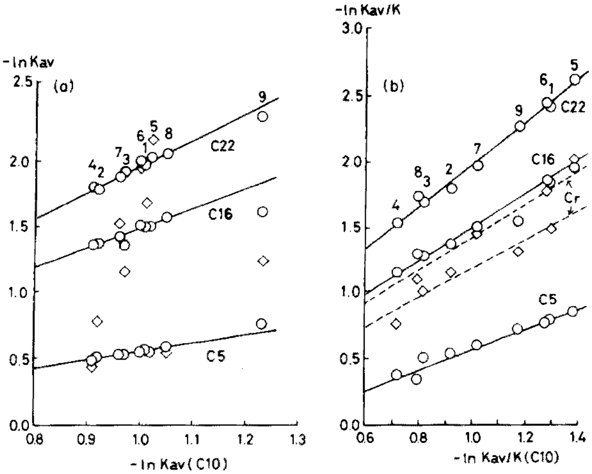


Fig. 9. Relationships between distribution coefficients of solutes and those of a reference solute in different solvents. (a) Plots of $-\ln K_{av}$ vs. $-\ln K_{av}(C_{10})$. (b) Plots of $-\ln K_{av}/K$ vs. $-\ln K_{av}/K(C_{10})$. Symbols and numbers correspond to those in Fig. 1 and Table 1, respectively. C_{10} is used as a standard solute. Solutes: —○— n-alkanes; —◇— Cr(AA)$_3$.

ln K_{av}/K values for metal acetylacetonates show good correlations with those for standard solutes but again different lines are given for aromatic hydrocarbons and chloroalkanes. This means that the interaction is estimated fairly well by the regular solutions treatment; the difference in interaction with aromatic hydrocarbons and chloroalkanes is much larger with metal acetylacetonates. In this case, β becomes too large ($\sim$ 1.6); the contribution of the gel matrix to the partition coefficients is overestimated, because the gel phase is considered as a kind of mixed solvent consisting of a solvent and the gel matrix. In the present calculations, kinetic effects and geometrical factors of solutes are not taken into consideration, and interactions of solutes with solvents and gels are estimated through only the

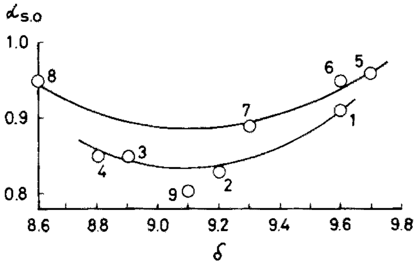


Fig. 10. Relations between values of α_{so} and solubility parameters of solvents. The numbering system for solvents follows Table 1.

solubility parameter. But the gel chromatographic behavior of metal acetylacetonates in various solvent systems is well explained by estimating the partition effect through the regular solutions treatment. The solubility parameters are useful as a criterion for choice of solvent in chromatographic systems with gels which interact weakly with solutes.

REFERENCES

1 Y. Yamamoto, E. Sumimura, K. Miyoshi and T. Tominaga, Anal. Chim. Acta, 64 (1973) 225.
2 Y. Yamamoto, T. Tarui, E. Iwamoto and T. Tarumoto, Anal. Chim. Acta, 84 (1976) 217.
3 Y. Yamamoto and T. Tarumoto, Anal. Lett., 3 (1970) 537.
4 Y. Yamamoto, M. Yamamoto, S. Ebisui, T. Takagi, T. Hashimoto and M. Izuhara, Anal. Lett., 6 (1973) 451.
5 (a) J. Porath, Pure Appl. Chem., 6 (1963) 233.
(b) A. G. Ogston, Trans. Faraday Soc., 54 (1958) 1754. T. C. Laurent and L. Killander, J. Chromatogr., 14 (1964) 317.
6 G. K. Ackers, Biochem. 3 (1964) 723.
7 J. N. Brönsted, Z. Phys. Chem. Bodenstein—Festband, (1931) 257.
8 E. F. Casassa, Sep. Sci., 6 (1971) 305.
9 J. F. K. Huber, F. C. Kraak and H. Veening, Anal. Chem., 44 (1972) 1554.
10 K. Saitoh, M. Satoh and N. Suzuki, J. Chromatogr., 92 (1974) 291.
11 T. L. Chang, Anal. Chim. Acta, 42 (1968) 51. W. W. Tau, J. Polym. Sci., Part A-2, 7 (1969) 483.
12 H. M. N. H. Irving, in J. A. Marinsky and Y. Marcus (Eds.), Ion Exchange and Solvent Extraction, Vol. 6, Marcel Dekker, New York, 1974, p. 140. H. M. N. H. Irving and J. S. Smith, J. Inorg. Nucl. Chem., 30 (1968) 1873.
13 A. E. Finn, G. C. Hampson and L. E. Sutton, J. Chem. Soc., (1938) 1254.
14 W. Heitz, Angew. Chem. Int. Ed. Engl., 9 (1970) 689.
15 J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes, 3rd edn., Dover, New York, 1964.
16 K. Saitoh and N. Suzuki, J. Chromatogr., 111 (1975) 29.

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AN EVALUATION OF SOME COMMERCIAL CADMIUM-SELECTIVE ELECTRODES

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SUMMARY

Three types of commercial cadmium-selective electrodes, Orion 94-48 A, Růžička Selectrode and TOA Cd-125, have been evaluated. Calibration curves were determined both in buffered and unbuffered cadmium ion solutions repeatedly during several weeks. Selectivities with respect to silver(I), copper(II), mercury(II), iron(II), iron(III), zinc(II) and lead(II), as well as the pH response, were determined by the mixed solution method. The response times of the electrodes were also studied.

A research program concerning the evaluation and development of ion-selective electrodes was started at the Technical Research Centre of Finland in 1972. Initially, the characteristics of four commercial sodium ion-selective electrodes were compared [1]. Later work has been concerned with the evaluation of commercial cadmium, lead, cyanide and nitrate electrodes. The present paper deals with the performance characteristics of cadmium-selective electrodes from three different manufacturers.

The cadmium-selective electrode is based on a membrane which consists of a mixture of cadmium sulfide with silver sulfide [2]. Similar ion-selective electrodes have been constructed for copper(II) and lead ions. Silver sulfide provides the necessary conductivity to the membrane while the silver ion activity at the membrane surface, which determines the potential of the electrode, is adjusted by the divalent metal ion activity in the sample through the appropriate solubility products [2].

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EXPERIMENTAL

Electrodes

Three different makes of electrodes were obtained and three of each kind were tested, altogether 9 electrodes. The electrodes and their numbering were as follows:

(1) Orion Research Inc. (U.S.A.), Cadmium electrode 94-48A: numbers 1, 2 and 3.

(2) Radiometer A/S, Denmark, Růžička Selectrode Kit 3012 with Cadmium Selectrode Power S 42115; numbers 4, 5 and 6.

(3) TOA Electronics Ltd., Japan, Cadmium electrode Cd-125: numbers 7, 8 and 9.

The Orion and TOA electrodes are of the solid-state type with membranes based on homogeneous precipitates. The Růžička Selectrode has a different structure [3]. The sensing surface of the Selectrode was cut clean according to the manufacturer's directions and covered with the electroactive compound sensitive to cadmium ion.

The reference electrodes used were a Radiometer saturated calomel electrode type K 401 and a Radelkis double-junction Ag/AgCl electrode type OP 820 with 0.1 M potassium nitrate solution in the outer chamber. The potential of the OP 820 electrode with respect to that of the K 401 was −7.3 mV. All potentials measured with the OP 820 were corrected to potential values on the K 401 scale. The reference electrodes were immersed directly in the test solutions.

Chemicals and equipment

All chemicals used were of analytical grade. The water used was distilled and deionized.

The following types of potentiometer were used: Radiometer PHM 64 digital pH/mV-meter, Orion 801 and 801A digital pH/mV-meters, Keithley 604 and 630 potentiometric electrometers and a Radiometer PHM 4c potentiometer. The stabilization of potentials was followed with a strip chart recorder, Honeywell Electronik 19 or Goerz Servogor RE 511. Solutions were stirred at constant speed with teflon-coated stirring rods.

Unless otherwise stated the ionic strength of the solutions was made up to 0.1 M with potassium nitrate.

RESULTS AND DISCUSSION

Calibration

The calibration of the electrodes was carried out either in cadmium ion buffer solution or in unbuffered solutions made by serial dilution.

Calibration in cadmium buffers. Cadmium ion buffer solutions were prepared as described by Růžička and Hansen [4]. The buffers used are given in Table 1. Two of each kind of electrode (all three of TOA) were used

TABLE 1

Cadmium ion buffers
(The ionic strength of all the buffers was 0.1 M (adjusted with KNO_3); for ML′ and L′ see ref. 4)

log [Cd^{2+}]	pH	pH buffer	Ligand	[ML′]/[L′]
4.84	4.55	acetate	NTA	1:1
5.73	4.60	acetate	NTA	1:10
6.80	6.51	maleate	NTA	1:1
7.97	6.68	maleate	NTA	1:10
10.23	9.21	borax	NTA	1:10
11.64	6.63	maleate	EDTA	10:1
12.65	6.64	maleate	EDTA	1:1
13.80	6.78	maleate	EDTA	1:10
15.29	9.16	borax	EDTA	1:1
16.32	9.19	borax	EDTA	1:10

for calibration. Before the measurements the electrodes were conditioned at least 24 h in solutions of 10^{-3} M cadmium nitrate at pH 3. The calibration procedure was repeated five times at intervals of two weeks. During the intervals the electrodes were stored in the conditioning solution. The Orion electrodes and the Selectrodes were investigated together in the same solution but the TOA electrodes were dealt with separately because they were obtained later.

Calibration was always started in the solutions with the lowest cadmium ion activity and proceeded towards higher activities. When the electrodes were transferred from one solution to the next they were blotted dry with tissue paper. Potentials were allowed to stabilize within 0.1 mV before readings were taken; at the lower concentrations stabilizations could take up to an hour. Measurements were made in a polyethylene vessel thermostatted at 298.1 K. The reference electrode was the K 401.

Calibration in unbuffered solutions. The solutions were prepared by serial dilution from a cadmium nitrate solution in water. The ionic strength was adjusted to 0.1 M by potassium nitrate, except for the solution of 0.1 M cadmium nitrate, the ionic strength of which was 0.4 M. Measurements were made without thermostatting at room temperature. The reference electrode was the OP 820. Three calibration runs were made with each electrode and the direction of concentration change was reversed after each run.

The electromotive force E of a cell consisting of a cadmium-selective electrode and a reference electrode at constant ionic strength can be written

$$E = E_{\text{const}} + S \log [\text{Cd}^{2+}] \qquad (1)$$

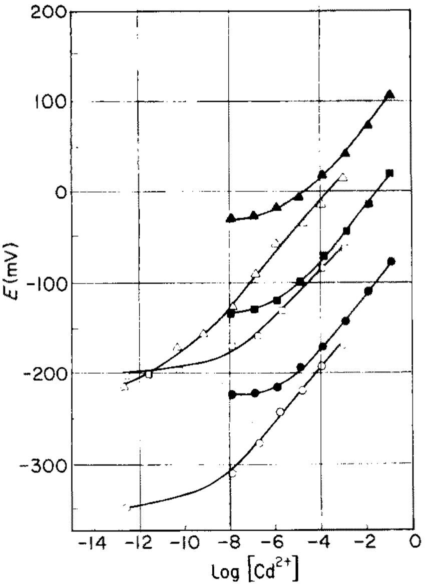
where E_{const} is a constant including the standard potential of the ion-selective electrode, the reference electrode potential, the liquid junction potential and the activity coefficient of the cadmium ion, S is the slope of the calibration graph with the theoretical value $RT \ln 10/zF$ or 29.6 mV at 298.1 K for a divalent cation.

Calibration curves obtained for the different electrodes by the above methods are compared in Fig. 1. Tables 2 and 3 show the parameters for the calibration graphs; the slopes were calculated from the linear portions. In unbuffered solutions points between log $[Cd^{2+}]$ -2 and -4 were used. In buffered solutions the calculations were made from experimental points between log $[Cd^{2+}]$ -6.8 and -3 for TOA electrodes, and between log $[Cd^{2+}]$ -10 and -3 for Orion and Selectrode electrodes. The electrodes in unbuffered solutions exhibited the theoretical slope within the limits of experimental error, but more varied results were obtained in the buffered solutions. Orion electrodes showed near ideal behaviour at the beginning of the experiment, but electrode 2, which was not treated in any way during the calibration series, showed a distinct drop in the value of the slope after two weeks, although this new value remained constant during the rest of the testing period. Electrode 9 was polished after the second calibration, according to the manufacturer's directions, and this resulted in an increase of the slope to give the theoretical value; afterwards a slight decrease in slope was found towards the end of the testing.

The Selectrodes also showed a nearly ideal slope at the beginning of the experiment though the S values were slightly lower than those of the Orion electrodes; again the slope decreased with time. The Selectrodes were polished before the last calibration but no improvement was found except that the confidence range narrowed. After the thin superficial layer of active material has deteriorated, apparently it can be restored only by renewing entirely. This is, of course, easily done with the Selectrode.

The TOA electrodes were calibrated in a separate testing series and were submitted also to other measurements during calibration. As a consequence there are rather large fluctuations in the slopes. Between the fourth and fifth calibration the electrodes were tested for interferences by Ag^+, Cu^{2+} and Hg^{2+} (No. 2 for Ag^+, No. 8 for Hg^{2+}, No. 9 for Cu^{2+}) which seems to have been especially harmful for the electrodes. After the fifth calibration the electrodes were polished thoroughly which markedly improved the performance characteristics.

The experimental values of the slope for the cadmium-selective electrodes seems to coincide with the theoretical value as long as the electrodes are fairly new, and this behavior has been confirmed by many authors [4—9]. However, this study indicates that the slope tends to decrease when the electrodes have been in use for some time and the S values seem to gather around 25 mV. Besides changes in the slopes of the calibration graphs, changes in the intercept potential, E_{const}, also proved the need for continual recalibration of an electrode. A stable value of E_{const} would be profitable but is in practice unattainable. The best behavior in this respect was shown by the Orion electrodes. But since a 30-mV or smaller change in the potential of an electrode equals a tenfold change in the concentration of cadmium ion, frequent recalibration is essential. As Tables 2 and 3 show, the electrodes



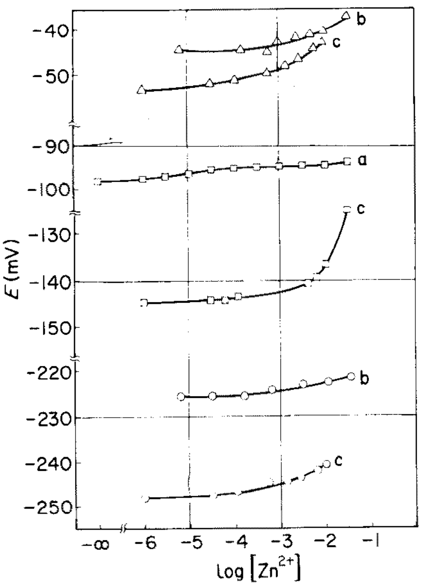


Fig. 1. Calibration graphs for cadmium electrodes. ○, Orion 94-48 A; △, Růžička Cadmium Selectrode; □, TOA Cd-125. Open symbols: buffered solutions (in Finland). Filled symbols: unbuffered solutions (in Hungary).

Fig. 2. Effect of zinc(II) on cadmium electrodes. ○, Orion 94-48 A; △, Růžička Cadmium Selectrode; □, TOA Cd-125; a, $[Cd^{2+}] = 10^{-4}$ M; b, $[Cd^{2+}] = 10^{-5}$ M; c, $[Cd^{2+}] = 10^{-6}$ M. Measurements made in Finland.

should be calibrated before each measuring series. Electrodes of the same make appear to have intercept potentials of the same magnitude, but differences between different makes are rather large. This is due to the different construction of the electrodes or different composition of the membranes.

The detection limit of an ion-selective electrode is defined in an IUPAC recommendation [10] * as the concentration of the ion of interest at which the potential of an ion-selective electrode deviates by $18/z_A$ mV from the extrapolated part of the linear (and presumably Nernstian) portion of the calibration curve. Detection limits determined for the electrodes tested, according to this definition, are also given in Tables 2 and 3. The values for the measuring range (which term is not exactly specified by any manufacturer) of the electrodes given by the manufacturers are as follows: for the Orion electrode, 10^{-1}—10^{-7} M; for the Selectrode, the same lower limit can be assumed [3]; for the TOA electrode, 10^{-2}—10^{-7} M. In unbuffered metal ion solutions obtained by serial dilution, the detection limit for an ion-selective electrode can be assumed to be 10^{-5}—10^{-6} M at most, because of difficulties in ensuring the concentration of a solution below this level.

Later this IUPAC recommendation has been cancelled but the detection limits determined according to it were left unchanged. The present valid IUPAC recommendation (Pure Appl. Chem. 1976, in press) uses the break point method. However, the values obtained by the two methods do not differ very much and the values reported give the correct magnitude of the detection limit.

TABLE 2

Calibration parameters for cadmium electrodes with 95 % confidence limits

Week	E_{const} (mV)	S(mV)	L.D.[c]	E_{const} (mV)	S(mV)	L.D.
Orion 94-48 A electrodes						
	No. 1[a]			No. 2[a]		
0	−84.1 ± 2.3	28.0 ± 0.4	9	−84.0 ± 4.0	28.2 ± 0.7	9.5
2	−85.3 ± 5.6	28.0 ± 1.0	9.5	−76.1 ± 6.5	29.0 ± 1.2	9.5
4	−82.8 ± 14.3	29.8 ± 3.2	10	−91.3 ± 8.0	25.8 ± 1.2	10.5
6	−77.4 ± 12.6	29.3 ± 1.9	10	−90.5 ± 5.7	25.9 ± 0.9	10.5
8	−86.0 ± 5.8	28.0 ± 0.9	10	−93.8 ± 15.7	25.1 ± 2.4	10
	No. 3[b]			No. 2[b]		
	−55.8 ± 4.3	30.5 ± 1.4	5.5	−56.5 ± 3.9	29.8 ± 1.3	5.5
Růžička Selectrodes						
	No. 5[a]			No. 6[a]		
0	94.1 ± 4.4	27.4 ± 0.7	10	103.9 ± 5.1	27.3 ± 0.8	9.5
4	133.0 ± 18.7	28.6 ± 2.9	10	136.4 ± 20.8	28.9 ± 3.2	10
6	133.5 ± 29.1	26.4 ± 4.5	10	139.9 ± 34.7	26.2 ± 5.3	10
8	113.4 ± 9.0	25.6 ± 1.4	10	117.4 ± 11.8	25.4 ± 1.8	10
	No. 4[b]			No. 6[b]		
	108.15 ± 6.6	28.8 ± 2.1	5.5	119.1 ± 14.9	28.2 ± 4.8	5

[a] In buffered solutions. [b] In unbuffered solutions. [c] Limit of detection, −log [Cd^{2+}].

TABLE 3

Calibration parameters for TOA Cd-125 electrodes[a]

Week	E_{const} (mV)	S(mV)	L.D.	E_{const} (mV)	S(mV)	L.D.
	Electrode 7			Electrode 8		
0	4.6 ± 6.2	24.3 ± 1.2	8	13.7 ± 7.9	25.1 ± 1.6	8
2	24.6 ± 33.8	30.2 ± 6.7	—[b]	38.8 ± 28.3	31.7 ± 5.6	—[b]
4	3.8 ± 12.1	25.2 ± 2.4	9	8.4 ± 27.9	24.9 ± 5.5	9
6	8.0 ± 13.6	24.2 ± 2.7	7	16.0 ± 15.4	27.0 ± 3.0	7
8[c]	−8.4 ± 8.8	21.1 ± 1.8	10	−19.2	17.8	4
10	5.2 ± 14.5	25.9 ± 3.1	9.5	1.7 ± 20.4	24.2 ± 4.4	9.5
[d]	35.7 ± 5.3	29.0 ± 1.7				
	Electrode 9					
0	6.1 ± 11.8	24.5 ± 2.3	7.5			
2	4.3 ± 17.6	20.1 ± 3.5	—[b]			
4	3.2 ± 16.9	24.9 ± 3.4	9			
6	−2.4 ± 7.5	22.2 ± 1.5	7			
8[c]	−19.6	17.7	4			
10	6.9 ± 17.9	26.1 ± 3.8	9.5			
[d]	26.6 ± 6.9	29.5 ± 2.2	5.5			

[a] For symbols see Table 2. [b] Calibration was not extended beyond the linear range. [c] See text. [d] In buffered solution.

Růžička and Hansen [4] have derived the expression

$$p[Cd^{2+}] = 1/2 \left[pK_{so} + \log \frac{\alpha Cd(OH)}{\alpha S(H)} \right] \quad (2)$$

where K_{so} is the solubility product of CdS and α denotes the side-reaction coefficients of Cd^{2+} and S^{2-} [11] for an electrode based on a CdS membrane. According to this expression, the detection limit is pH-dependent. At pH values between 6 and 10, detection limits from 10^{-9}—10^{-11} M, respectively, were found. The detection limits obtained in this work confirm these considerations. In unbuffered solutions the detection limits found are between 10^{-5} M and 10^{-6} M. In buffered solutions, the values obtained go down to $10^{-10.5}$ M, and the Orion electrodes and Selectrodes are of the same quality in this respect. No decrease in the sensitivity was found during the calibration period although the slope and standard potential both changed. Only slightly lower detection limits were obtained with the TOA electrodes at their best, though in most measurements the limit was lower, possibly because of the varied measurements to which these electrodes were subjected. Experiences with the TOA electrode showed that the electrode parameters change rather easily and care must be exercised during measurements not to expose the electrodes to harmful interferences.

Selectivity measurements

The IUPAC recommendation [10] for the definition of the selectivity coefficient is given by the modified Nernst equation

$$E = E_{const} + \frac{RT}{z_A F} \ln \left[a_A + k_{A,B} a_B^{z_A/z_B} \right] \quad (3)$$

where subscript A stands for the primary ion, B for the interfering ion, a is activity, $k_{A,B}$ is the selectivity coefficient, and other symbols have their usual meaning.

Determination of selectivity coefficients was made by the mixed solution method [12]. The concentration of the primary ion was kept constant and that of the interfering ion was gradually increased by adding the appropriate titrant from a burette to the cell. After each addition the potential was allowed to stabilize. The results were presented graphically and the selectivity coefficients were determined either by the break-point method or by the computation method of Srinivasan and Rechnitz [13] which employs the expression

$$k_{A,B} = \left(a_A \exp \frac{E' - E}{RT/z_A F} - a'_A \right) \Big/ \quad a'_B \quad (4)$$

where a and E refer to quantities in a pure solution of A and the primed symbols to quantities in mixed solution of A and B. In our measurements a_A is equal to a'_A. The activity coefficients were calculated as described by Kielland [14].

Selectivities were determined for Ag^+, Cu^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, and H^+ (pH dependence). Measurements of selectivity to Ag^+, Hg^{2+} and Cu^{2+} were carried out in a solution 10^{-2} M with respect to cadmium ion. Copper and mercury interferences were measured at pH 2. No stable potentials were obtained with these interferents. At a concentration of 10^{-7} M of the interferents, the potential of the cadmium electrodes began to rise steeply. Figure 2 shows the effect of zinc(II). Measurements were made at various concentrations of cadmium(II). The selectivity coefficients $k_{Cd,Zn}$ obtained are given in Table 4.

For the determination of the interferences by iron(II), solutions were made up from $Fe(NH_4)_2SO_4$, H_2SO_4 ($5 \cdot 10^{-3}$ M), $Cd(NO_3)_2$ (10^{-4} M), and KNO_3 (0.1 M); the pH was about 2.1. Results are presented in Fig. 3 and Table 4. The selectivity to iron(III) was measured in solutions of $Fe(NO_3)_3$ acidified to pH 2 with nitric acid. Results are shown in Fig. 4.

Interference by lead(II) was measured at various concentrations of cadmium(II) and the curves obtained in 10^{-4} M cadmium solutions are presented in Fig. 5. Selectivity coefficients determined by the break-point method are presented in Table 4.

The effect of pH was studied by a titration procedure. The starting solution was 10^{-2} M, 10^{-3} M or 10^{-4} M with respect to cadmium ion and the pH was 2 (adjusted with nitric acid). To this solution was added sodium hydroxide solution of such high concentration that the volume of the cadmium solution did not change noticeably. The potential—pH curves are shown in Fig. 6.

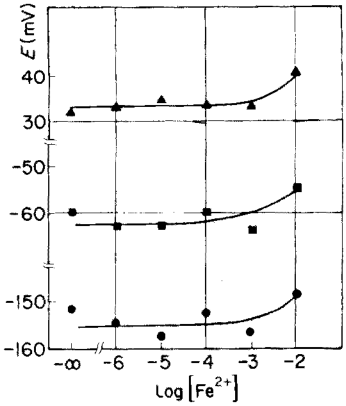
In general, cadmium electrode interferences are caused by cations which form sulfides less soluble than CdS. Pungor and Tóth [15] have derived an expression for the selectivity coefficient of precipitate-based ion-selective

TABLE 4

Experimental selectivity coefficients

Interfering ion	$[Cd^{2+}]$	Orion	Selectrode	TOA
Zn^{2+}	10^{-2}	no interference	no interference	no interference
	10^{-4}	—	—	$7.8 \cdot 10^{-4}$[b]
	10^{-5}	$9.5 \cdot 10^{-5}$[a]	$2.3 \cdot 10^{-4}$[a]	
	10^{-6}	$6.8 \cdot 10^{-5}$[a]	$1.1 \cdot 10^{-4}$[a]	$1.5 \cdot 10^{-4}$[b] ($1.1 \cdot 10^{-4}$[a])
Fe^{2+}	10^{-4}	≅0.002[a]	≅0.003[a]	≅0.003[a]
Pb^{2+}	10^{-2}	—	—	0.5
	10^{-3}	7.1	5.4; 21.8[c]	
	10^{-4}	0.6; 0.4; 0.6; 1.8[c]	0.2; 1.2; 0.7; 0.4[c]	4.8; 1.6[c]

[a] Determined by computation. [b] Determined by the break-point method. [c] Measured in Hungary; the other measurements were made in Finland.



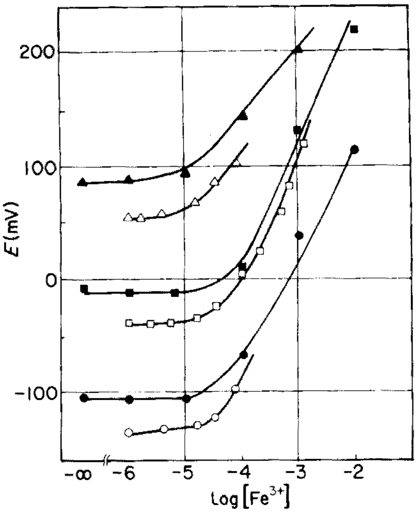


Fig. 3. Effect of iron(II) on cadmium electrodes. ●, Orion 94-48 A; ▲, Růžička Cadmium Selectrode; ■, TOA Cd-125; $[Cd^{2+}] = 10^{-4}$ M. Measurements made in Hungary.

Fig. 4. Effect of iron(III) on cadmium electrodes. ○, Orion 94-48 A; △, Růžička Cadmium Selectrode; □, TOA Cd-125. Open symbols: measurements made in Finland. Filled symbols: measurements made in Hungary. $[Cd^{2+}] = 10^{-2}$ M.

electrodes, which written for a cadmium sulfide membrane electrode, is

$$k_{\mathrm{Cd,B}} = K_{\mathrm{so}}(\mathrm{CdS})/K_{\mathrm{so}}(\mathrm{B}_n\mathrm{S}_m)^{1/m} \qquad (5)$$

where B stands for the interfering cation and K_{so} is the solubility product of the appropriate sulfide.

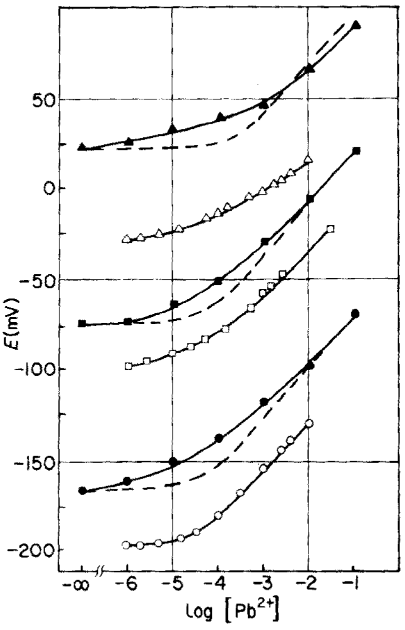
For the electrodes tested, the manufacturers state the following selectivity data.

Orion. Cu^{2+}, Hg^{2+} and Ag^{+} must be absent; Fe^{3+} and Pb^{2+} interfere if the level of these ions exceeds the level of cadmium ion in the solution.

Radiometer. Heavy metal ions will interfere with increasing severity in the following order of progression: Sn^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}, Ag^{+}. Ag^{+} and Hg^{2+} must not be present in detectable amounts.

TOA. The following selectivity coefficients are given (valid at 10^{-2} M solution of Cd^{2+}): Pb^{2+}, Cu^{2+}, Fe^{2+}, 1; Cr^{3+}, 10^{-2}; Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Al^{3+}, 10^{-5}; Hg^{2+} and Ag^{+} must be absent.

Listed in Table 5 are theoretical coefficients (calculated from eqn. 5) and also some experimental values found in the literature. Theory predicts very severe interferences by Ag^{+}, Cu^{2+}, and Hg^{2+} and this was confirmed by our measurements. The concentration of these interferents must be below 10^{-7} M when the cadmium ion concentration is 10^{-2} M. This fact is also stated by the manufacturers except that Radiometer and TOA have



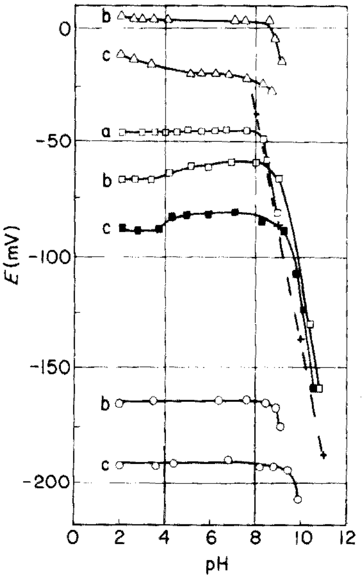


Fig. 5. Effect of lead(II) on cadmium electrodes. ○, Orion 94-48 A; △, Růžička Selectrode; □, TOA Cd-125. Open symbols: measurements made in Finland. Filled symbols: measurements made in Hungary. [Cd^{2+}] = 10^{-4} M

Fig. 6. pH response of cadmium electrodes. ○, Orion 94-48 A; △, Růžička Selectrode; □, TOA Cd-125; +, calculated points; a, [Cd^{2+}] = 10^{-2} M; b, [Cd^{2+}] = 10^{-3} M; c, [Cd^{2+}] = 10^{-4} M.

TABLE 5

Selectivity coefficients for cadmium-selective electrodes

Interfering ion B	Calculated value[a] $k_{Cd,B}$	Literature value (experimental)	
		$k_{Cd,B}$	Ref.
Ag^+	$10^{22.9}$	—	
Cu^{2+}	$10^{9.1}$	—	
Hg^{2+}	$10^{25.7}$	—	
Zn^{2+}	0.005	$4.14 \cdot 10^{-11}$	6
		10^{-4}	5
Fe^{2+}	$1.3 \cdot 10^{-9}$	196	6
Fe^{3+}		300	5 ([Fe^{3+}] = 10^{-3} M)
		400	5 ([Fe^{3+}] = 10^{-4} M)
Pb^{2+}	3.2	6.1	6
		0.5	5

[a] According to eqn. (5); solubility products from [11].

underestimated the effect of copper(II). The measured interference by zinc(II) is about ten times smaller than the calculated interference. The effect is so small that only in one case (TOA at 10^{-6} M Cd^{2+}) could the break-point method be employed; in other cases eqn. (4) was used. (When there was no experimental value for E in pure cadmium(II) solution, then the value at the lowest concentration of zinc(II) was used instead.) Though the curves in Fig. 2 do not seem to give a firm basis for the determination of the selectivity coefficients, the results are all of the same magnitude and in agreement with the literature values. However, the tabulated values of the solubility products of sulfides may not be directly applicable to the conditions under which the selectivity coefficients were determined. A similar phenomenon has been reported in connection with the detection limit of the fluoride electrode [2].

Interference by iron(II) is also so small that the selectivity coefficient can hardly be determined. The values are much larger than predicted by eqn. (5), but their significance is small. Some workers [6] have found great interference from iron(II), but this may be accounted for by the presence of iron(III), the absence of which in the present study was ensured by using Mohr's salt in acidic media and in some experiments by using nitrogen to purge solutions.

The influence of iron(III) on the cadmium electrodes was very severe. Even the smallest concentrations of iron(III) in a solution resulted in a drifting potential; at higher concentrations drifting was very rapid. For this reason, selectivity coefficients were not calculated. The effect of iron(III) has been explained by its oxidizing properties [5, 6]. In spite of this, the manufacturers have not included it among the serious interferents, possibly because it can obviously be masked by raising the pH of the sample, as stated by Orion. At pH 2 the concentration of iron(III) must be less than 10^{-5} M when the concentration of cadmium(II) is 10^{-2} M.

The solubility products of cadmium sulfide and lead sulfide are of about the same magnitude and the electrodes were fairly stable in the presence of lead(II). Though the values obtained for the selectivity coefficients vary somewhat they are of the same magnitude as predicted by theory and found by other workers. The use of eqn. (3) for the calculation of selectivity coefficients presupposes that an electrode has the same calibration slope for the interferent ion as for the primary ion if their valencies are the same. However, the right-hand portions of most curves in Fig. 5 are not linear, so that eqn. (3) cannot represent them precisely. To check this the selectivity coefficients in eqn. (3) were given appropriate values from Table 4 and the mixed solution potentials were calculated and plotted. These curves are represented by the broken lines in Fig. 5. The intercept potential was given an arbitrary value in each case so that experimental and theoretical curves coincided at the left-hand end. There are rather large differences between the curves, and apparently the slope determined experimentally for the lead ion is not the same as for the cadmium ion. The fit could be improved by applying a different slope for the lead ion [16, 17].

The pH is expected to affect the cadmium electrodes in two ways. At low pH values the solubility of metal sulfides increases because of the formation of HS^- and H_2S which results in a rise of potential [2]. At high pH the precipitation of $Cd(OH_2)$ decreases the concentration of cadmium in the solution and the potential decreases. However, there is no rise of potential to be seen at low pH values (Fig. 6); obviously this effect appears only at lower concentrations of cadmium ion than were used in these experiments. The descending part of the curve at higher pH can be calculated from

$$E = E_{\text{const}} + S \log \frac{K_{\text{so}}}{y_{\text{Cd}^{2+}} K_{\text{w}}^{2}} - 2\,S\,\text{pH} \tag{6}$$

where K_{so} is the solubility product of cadmium hydroxide ($\log K_{\text{so}} = -14.09$ [18]), $y_{\text{Cd}^{2+}}$ is the activity coefficient of the cadmium ion and, K_{w} is the ion product of water. The calculated line for a TOA electrode at concentration 10^{-2} M is represented by a broken line in Fig. 6. The agreement between the theoretical and experimental curves is good.

On the basis of Fig. 6, it appears that cadmium electrodes can be used below pH 8 without the risk of hydrolysis of the cadmium ion. The electrode also measures the activity of cadmium ion in the solution beyond this pH value.

Response times

Response times of the electrodes were measured by the apparatus described by Tóth and Pungor [19]. Electrodes were subjected to changes in concentration from 10^{-4} M to 10^{-2} M with respect to cadmium ion and vice versa. Typical oscillograph traces are shown in Fig. 7. The Orion and TOA electrodes have about the same response time, the TOA electrode being perhaps a bit slower. The Růžička Selectrode showed markedly (about 5—10 times) slower potential vs. time response than the other types. This may be due to its less dense surface structure which slows up concentration changes. All electrodes show faster response when going from lower to higher concentration than in the opposite direction. The effects of flow rate and the ionic strength were also studied. Slow flow rates gave a sluggish response but when the flow rate exceeded a certain critical value, the response time showed no flow-rate dependence. In the presence of 0.1 M KNO_3 the

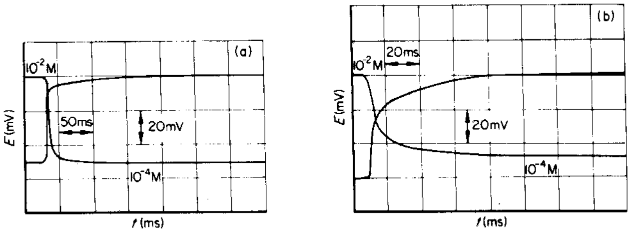


Fig. 7. Response time measurements for cadmium electrodes. a, Orion 94-48 A; b, TOA Cd-125. 10^{-2} M ⇌ 10^{-4} M Cd^{2+}.

cadmium response-time curves were as obtained for other solid-state electrodes, while in the absence of KNO_3 the potential overshot in the first one or two milliseconds.

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REFERENCES

1 M. F. Wilson, E. Haikala and P. Kivalo, Anal. Chim. Acta, 74 (1975) 395, 411.
2 J. Ross, in R. Durst (Ed.), Ion-selective Electrodes, N.B.S. Special Publication No. 314, U.S. Government Printing Office, Washington, 1969.
3 J. Růžička and G. G. Lamm, Anal. Chim. Acta, 53 (1971) 206.
4 J. Růžička and E. Hansen, Anal. Chim. Acta, 63 (1973) 115.
5 M. Mascini and A. Liberti, Anal. Chim. Acta, 64 (1973) 63.
6 M. Brand, I. Militello and G. Rechnitz, Anal. Letters, 2 (1969) 523.
7 H. Hirata and K. Date, Bull. Chem. Soc. Jpn., 46 (1973) 1468.
8 H. Hirata and K. Higashiyama, Talanta, 19 (1972) 391.
9 J. Czaban and G. Rechnitz, Anal. Chem., 45 (1973) 471.
10 IUPAC Information Bulletin. Appendices on provisional nomenclature, symbols, units, and standards No. 43, Recommendation for Nomenclature of Ion-selective Electrodes, January 1975.
11 A. Ringbom, Complexation in Analytical Chemistry, Interscience, New York, 1963, Ch. II.
12 G. Moody and J. Thomas, Selective Ion-sensitive Electrodes, Merrow, Watford, 1971.
13 K. Srinivasan and G. Rechnitz, Anal. Chem., 41 (1969) 1203.
14 J. Kielland, J. Am. Chem. Soc., 59 (1937) 1675.
15 E. Pungor and K. Tóth, Anal. Chim. Acta, 47 (1969) 291.
16 M. S. Mohan and G. A. Rechnitz, Anal. Chem., 45 (1973) 1323.
17 E. Hakoila, U. Lukkari and I. Mannonen, Suomen Kemistilehti, 46B, (1973) 344.
18 L. Sillén and A. Martell, Stability Constants of Metal-ion Complexes, Chem. Soc. Special Publ. No. 25, London, 1971.
19 K. Tóth and E. Pungor, Anal. Chim. Acta, 64 (1973) 417.

Analytica Chimica Acta, 87 (1976) 401—409

AN EVALUATION OF SOME COMMERCIAL LEAD(II)-SELECTIVE ELECTRODES

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SUMMARY

Two types of commercial lead(II)-selective electrode, the Orion 94-82 and the Růžička lead Selectrode, are compared. Calibration curves were determined in both buffered and unbuffered lead-ion solutions repeatedly for several weeks. Selectivities with respect to copper(II), silver(I), mercury(II), iron(III), zinc and cadmium were examined as well as the pH response by the mixed solution method. The response times of the electrodes were also studied.

The results of an evaluation of some cadmium ion-selective electrodes were reported recently [1]. This report gives corresponding results for lead-selective electrodes; the testing program followed the same scheme as applied previously.

The lead(II)-selective electrode incorporates a solid-state membrane which is usually a mixture of silver sulfide and lead sulfide [2]; analogous construction has been employed for copper and cadmium ion-selective electrodes. The mechanism of the electrode function has been discussed by Ross [2]. The membrane can be prepared from the sulfide mixture by a variety of methods; for examples, homogeneous membranes have been prepared by pressing [2—6], pressing and sintering [7, 8], or melting [9]. Heterogeneous membranes have been prepared by incorporating the sulfide mixture into a silicone rubber [10] or polyethylene [11] matrix. Monocrystal membranes have been prepared from a synthetic lead chalcogenide [12, 13]. Instead of sulfides, tellurides or selenides [5] can be used for membrane material. Precipitate-based electrodes can also be prepared by applying the precipitate to the end of a hydrophobized teflon rod [14, 15]. Lead ion-selective electrodes based on different liquid ion exchangers have also been developed [16—19].

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The lead electrode can be used for direct potentiometric determination of lead ions but it has been used most frequently as an indicating electrode in potentiometric titrations. The applications include titration of lead with Na_2EDTA [12, 13], titration of sulfate, oxalate, hexacyanoferrate(II), tungstate, pyrophosphate and chromate with the Růžička Selectrode [14] or the polyethylene heterogeneous membrane electrode [11], titration of sulfate with lead perchlorate [20, 21], titration of lead in aqueous or non-aqueous solutions [22], and determination of sulfur by titration with lead perchlorate in various substances [23, 24, 25] after conversion to sulfate. Selig [26] has discussed the use of dioxane in titrations with a lead(II)-selective electrode.

EXPERIMENTAL

Electrodes

Two kinds of lead-selective electrodes were tested, three electrodes of each kind:

(i) Orion Research Inc., lead electrode 94-82, designated Orion 1, 2 and 3.
(ii) Radiometer A/S, Růžička Selectrode Kit 3012, with lead Selectrode powder S 42215, designated Selectrode 1, 2 and 3.

The reference electrodes used were an Orion double-junction electrode 90-02 with 10 % potassium nitrate solution in the outer chamber, and two Radelkis calomel reference electrodes OP 810. The Orion reference electrode was immersed directly in the test solution whereas the Radelkis reference electrodes were connected to the test solution by a salt bridge of 0.1 M potassium nitrate in agar-agar.

Chemicals and equipment

Chemicals were of analytical reagent grade. The water used was distilled and deionized. Instruments and conditions were the same as before [1].

RESULTS AND DISCUSSION

Calibration

Calibrations were done by the same method as for the cadmium electrodes, i.e. both in lead ion buffer solutions and in unbuffered solutions made by serial dilution. Lead ion buffer solutions were prepared as described by Hansen and Růžička [15]; the characteristic values of the buffer solutions are given in Table 1. Unbuffered solutions were made from lead nitrate. The ionic strength of all the solutions was adjusted to 0.1 M by potassium nitrate except in 0.1 M lead nitrate solution where the ionic strength was 0.4 M. Unbuffered solutions in which the concentration of lead ions was 10^{-4} M or less were prepared, stored and handled in polyethylene flasks and beakers.

Two electrodes of each kind were used for calibration. Before the first calibration the electrodes were treated as recommended by the manufacturers. Calibration was repeated several times at certain time intervals. Between the

TABLE 1

Lead ion buffer solutions

(For [L′] and [PbL′] see ref. 14.)

Solution no.	Ligand (L)	[L′]/[PbL′]	pH-Buffer	pH	—log [Pb^{2+}]
I	EDTA	1:10	Borax	8.49	15.1
II	NTA	10:1	Borax	9.07	12.0
III	NTA	1:1	Borax	9.02	10.9
IV	NTA	1:10	Borax	8.44	9.4
V	NTA	1:1	Maleate	6.54	8.5
VI	NTA	1:10	Maleate	4.78	5.8
VII	NTA	1:10	Acetate	4.29	5.3
VIII	—		—		4.0[a]
IX	—		—		3.0[a]

[a]Made by serial dilution.

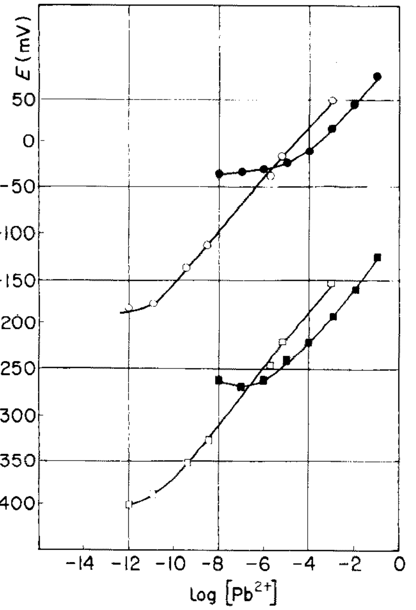

Fig. 1. Calibration graphs for lead(II)-selective electrodes. ○ Růžička Selectrode in metal buffer solutions; ● Růžička Selectrode in unbuffered solutions; □ Orion electrode in metal buffer solutions; ■ Orion electrode in unbuffered solutions.

calibrations the electrodes were stored in a conditioning solution (10^{-3} M lead nitrate, pH 3).

Typical calibration curves are shown in Fig. 1 and numerical values of the calibration parameters are presented in Table 2. From Fig. 1 one can see the

TABLE 2

Calibration parameters for lead(II)-electrodes with 95 % confidence limits

Week	No. 1			No. 2		
	E_c(mV)	S(mV)	L.D.[a]	E_c(mV)	S(mV)	L.D.
Orion 94-82						
0	—64.2 ± 21.0	30.9 ± 3.1	11	—69.6 ± 25.8	30.9 ± 3.8	10.5
2	—93.3 ± 45.2	23.2 ± 8.0	9	—96.8 ± 11.4	24.9 ± 2.0	8.5
4	—89.9 ± 13.1	25.7 ± 2.0	10	—87.4 ± 1.1	28.2 ± 0.2	11
6	—79.6 ± 10.3	27.2 ± 1.6	10.5	—78.9 ± 5.0	29.1 ± 0.8	11.5
8	—79.0 ± 10.3	26.6 ± 1.7	10.5	—77.5 ± 2.1	29.0 ± 0.3	11
8[b]	—86.2 ± 14.2	28.2 ± 2.2	10.5	—83.2 ± 4.4	29.2 ± 0.7	11
8[c]	—102.8 ± 4.0	29.5 ± 1.3	5.5			
Růžička lead Selectrode F 3012						
0	129.3 ± 12.8	28.3 ± 1.7	11	126.9 ± 13.1	27.9 ± 1.7	11
2	112.5 ± 7.7	27.1 ± 1.1	11.5	113.1 ± 14.1	28.1 ± 2.0	11.5
4	106.3 ± 10.0	25.5 ± 1.6	11	101.8 ± 6.1	24.6 ± 0.9	10.5
6	105.2 ± 13.8	23.6 ± 2.4	10.5	104.3 ± 5.3	23.8 ± 0.8	10.5
8	102.5 ± 8.1	21.8 ± 1.3	10.5	103.8 ± 7.2	23.2 ± 1.1	10.5
8[b]	106.4 ± 6.1	24.4 ± 1.0	11	110.5 ± 8.3	25.7 ± 1.3	11.5
8[c]	95.3 ± 7.8	26.7 ± 2.5	4.8			

[a] Limit of detection, —log [Pb^{2+}]. [b] After polishing the electrodes. [c] In unbuffered solutions, three measurements at each concentration; all the other measurements in buffered solutions.

basic difference between the behaviour of the electrodes in buffered and unbuffered solutions. The limit of detection determined according to the definition by IUPAC [27] * is considerably smaller in unbuffered solutions. Calculation of the limit of detection by the equation derived by Hansen and Růžička [14] gives a value of 7.5 at pH 4 and a value of 11.8 at pH 9 for the quantity —log [Pb^{2+}]. It can be seen that the limit of detection in buffered solutions is in good agreement with the predicted values. In contrast, in unbuffered solutions made by serial dilution, the limit of detection is mostly determined by the fact that concentrations below ca. 10^{-5} M cannot be reliably controlled. The intercept potential [1] E_c and slope S in the Nernst equation

$$E = E_c + S \log c_{Pb^{2+}} \tag{1}$$

were calculated by regression analysis from the linear parts of the calibration curves. The theoretical value for S at 298.1 K for a divalent cation is 29.6 mV. In buffered solution the Orion electrodes showed over-Nernstian slope in the first measurement after which a sudden decrease was found in all calibration parameters. In the subsequent measurements the values gradually increased and the electrode No. 2 showed finally almost Nernstian behaviour. Conditions

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*See page 391 of previous article, Anal. Chim. Acta, 87 (1976) 387.

were kept constant during the whole calibration study and the deviating results in the second calibration cannot be explained. The slopes for the Růžička Selectrodes were below the Nernstian value in every calibration, the best value being obtained in the beginning. During the course of the test series a considerable decrease in the values of slopes was found.

The difference in E_c values between the two types of electrodes was almost 200 mV but the differences in E_c values between electrodes of the same kind were less than 5 mV in all calibrations though the absolute E_c values changed with time. The limit of detection of all the electrodes remained fairly constant and the value was near the theoretical value as well as in agreement with the values given by the manufacturers.

After the fifth calibration the membranes of all electrodes were polished with Orion abrasive strips and the results are also shown in Table 2. A slight improvement in the slopes of all electrodes can be seen. Růžička Selectrodes, however, cannot be polished very vigorously because of the thin and comparatively loose layer of the active material. The performance of an old Růžička Selectrode is best improved by renewing the surface entirely, which is readily accomplished.

These results show that calibration parameters change with time so the user of these electrodes must ensure that calibration is done at suitable time intervals.

Selectivity

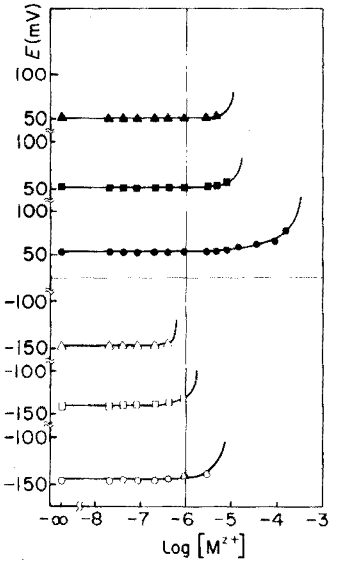
The selectivity of the lead(II) electrodes was determined with respect to Ag^+, Mg^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+} and H^+ ions by the mixed solution method [1, 28] with the primary ion concentration fixed. Solutions were made up from nitrates of the appropriate metal ion, a titration procedure was used and the initial solution contained lead nitrate and potassium nitrate. In the case of copper(II), mercury(II) and iron(III) solutions, the pH was adjusted to 2 with nitric acid to prevent hydrolysis. Titrants contained the same components as the respective initial solutions and the interfering ion at an appropriate concentration level. The ionic strength was always 0.1 M. The results are shown graphically in Figs. 2—5.

As expected, on the basis of the solubility products of the metal sulfides, the effects of silver(I), copper(II) and mercury(II) ions are very severe, the interference increasing in the same order as the solubility products decrease. Figure 2 shows that for the Orion lead(II)-selective electrode, the lowest allowable value of the quantity $-\log c$ is about 6.5 for mercury(II) and silver(I) and 5.5 for copper(II). The corresponding values for the Růžička Selectrode are about 5.5 and 4, respectively, i.e. this electrode tolerates these interferents over ten times better. These results are in agreement with the information given by Orion Research Inc. [29].

With respect to iron(III), Orion Research states that interference occurs only when the concentration of iron(III) exceeds that of lead ions. Radiometer gives no information about the effect of iron(III). Mascini and Liberti

[11] found quite severe interference by iron(III) at pH 1 for the heterogeneous lead electrode they developed; our results, shown in Fig. 3, confirm the results of Mascini and Liberti. The interference begins at about 10^{-5} M iron(III) and seems to be rather independent of the lead(II) concentration; the curves extend to the point at which a stable potential could still be obtained. Beyond these points the potential of an electrode did not stabilize at all but rose at a constantly increasing rate. The effect of iron(III) on both lead electrodes and cadmium electrodes is very similar.

The theoretical value [30] of the selectivity coefficient of the lead(II)-selective electrode with respect to cadmium ion, $k_{\mathrm{Pb,Cd}}$, as calculated from the solubility products of the corresponding sulfides is 0.32. This value suggests a moderate interference by cadmium. Experimental results are shown in Fig. 4 and the form of the curves allows the determination of the selectivity coefficient by the break-point method [28]. The coefficients thus calculated are given in Table 3; all the values are smaller than the theoretical value. The Selectrode seems to be somewhat less sensitive to cadmium ion than the Orion electrode and the modified Nernst equation [27] is more closely followed by lead electrodes in the presence of cadmium ions than by cadmium electrodes in the presence of lead ions [1].



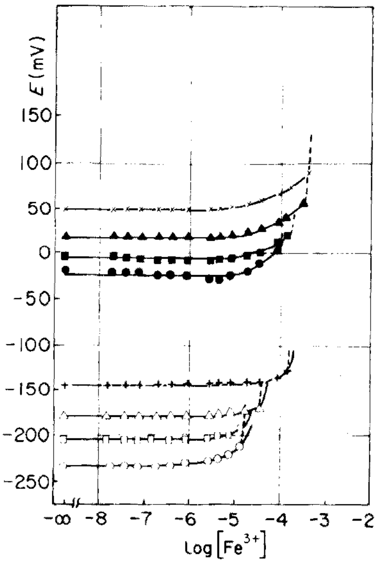
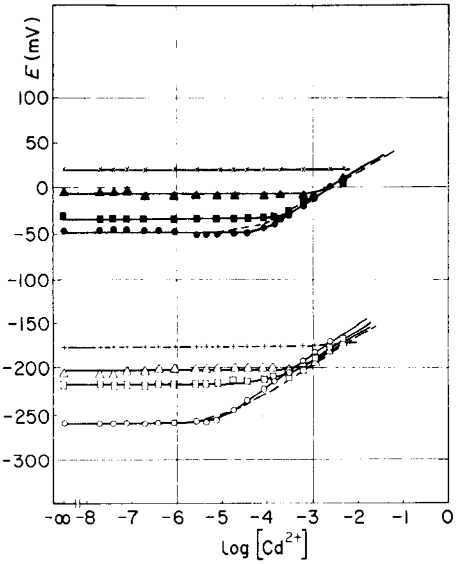


Fig. 2. Effect of copper(II), silver(I) and mercury(II) on lead electrodes. Closed symbols for Růžička Selectrode, open symbols for Orion electrode; ▲ and △ for Hg^{2+}; ■ and □ for Ag^+; ● and ○ for Cu^{2+}. Lead(II) background concentration, 10^{-2} M.

Fig. 3. Effect of iron(III) on lead electrodes, at various lead(II) concentrations. Closed symbols and × for Růžička Selectrode, open symbols and + for Orion electrode: × and + 10^{-2} M Pb^{2+}; ▲ and △ 10^{-3} M Pb^{2+}; ■ and □ 10^{-4} M Pb^{2+}; ● and ○ 10^{-5} M Pb^{2+}.



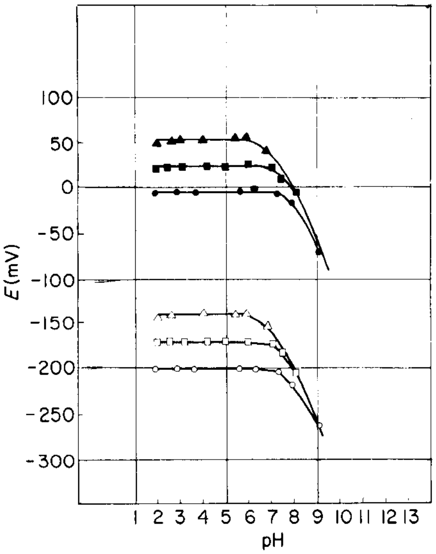


Fig. 4. Effect of cadmium(II) on lead electrodes at various lead(II) concentrations. Closed symbols and × for Růžička Selectrode, open symbols and + for Orion electrode; × and + 10^{-3} M Pb^{2+}; ▲ and △ 10^{-4} M Pb^{2+}; ■ and □ 10^{-5} M Pb^{2+}; ● and ○ 10^{-6} M Pb^{2+}. Dashed lines represent the theoretical response as calculated by the modified Nernst equation in 10^{-6} M Pb^{2+} solution.

Fig. 5. Effect of pH on lead electrodes at various lead(II) concentrations. Closed symbols for Růžička Selectrode, open symbols for Orion electrode; ▲ and △ 10^{-2} M Pb^{2+}; ■ and □ 10^{-3} M Pb^{2+}; ● and ○ 10^{-4} M Pb^{2+}.

TABLE 3

Experimental selectivity coefficients $k_{Pb^{2+},Cd^{2+}}$

$[Pb^{2+}]$ (M)	Type of electrode	
	Orion 94-82	Růžička lead Selectrode
10^{-6}	0.12	0.012
10^{-5}	0.045	0.051
10^{-4}	0.18	0.064

Zinc(II) had a rather small effect on the cadmium electrodes [1]; their effect on lead electrodes was found to be completely insignificant. Measurements were carried out by the mixed solution method with a fixed background concentration of lead ions; the concentration levels were 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} M.

The pH response of the lead electrodes was determined by adding 10 M sodium hydroxide solution with a microsyringe to a lead(II) solution, the pH of which was initially 2 (adjusted by nitric acid). The potential-pH curves are given in Fig. 5. The predicted rise in potential at low pH values is not observed. Change in pH has no effect on the potential of lead electrodes until the value is reached where the precipitation of lead hydroxide begins. This value is about pH 6 in 10^{-2} M lead ion solution and pH 7 in 10^{-4} M solution. The values are lower than those found for cadmium electrodes, reflecting the difference in the solubility products of the respective hydroxides.

Response times

The response times of the lead electrodes were investigated as described by Tóth and Pungor [31]. A typical oscilloscope curve is shown in Fig. 6. A marked difference was found between the Orion and the Růžička type electrodes; the Orion electrode responds about 5 to 10 times faster than the Růžička electrodes. A similar difference between these two types of electrodes was found earlier with the cadmium electrodes [1]; this is probably due to the preparation of the electrodes.

The authors wish to thank Radiometer A/S and Orion Research Inc. for providing the electrodes at a reduced price.

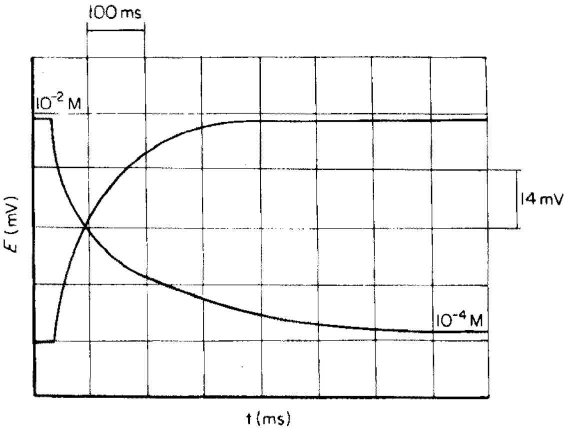


Fig. 6. Response time measurements with a Růžička-type electrode. $c = 10^{-2}$ M $\rightleftharpoons$ 10^{-4} M.

REFERENCES

1 P. Kivalo, E. Pungor, G. Sundholm, K. Tóth, R. Virtanen, K. Wickström and M. Wilson, Anal. Chim. Acta, 87 (1976) 387.
2 J. Ross, in R. Durst (Ed.), Ion-selective Electrodes, NBS Special Publication No. 314, U.S. Government Printing Office, Washington, D.C., 1969, p. 80.
3 M. Koebel, Anal. Chem., 46 (1974) 1559.
4 H. Tompson and G. Rechnitz, Chem. Instrum., 4 (1972) 239.
5 K. Higashiyama and H. Hirata, Deutsches Patentamt, Offenlegungsschrift 2210525, KL. 42 1, 3/06, 2. Nov. 1972.

6 J. Czaban and G. Rechnitz, Anal. Chem., 45 (1973) 471.
7 H. Hirata and K. Higashiyama, Talanta, 19 (1972) 391.
8 H. Hirata and K. Higashiyama, Anal. Chim. Acta, 54 (1971) 415.
9 A. Gordievskii, V. Shterman, A. Syrchenkov, N. Savin, A. Zkukov and Yu. Urosov, Zh. Anal. Khim., 27 (1972) 2170.
0 H. Hirata and K. Date, Anal. Chem., 43 (1971) 279.
1 M. Mascini and A. Liberti, Anal. Chim. Acta, 60 (1972) 405.
2 D. Cörmös, I. Haiduc and P. Stetin, Rev. Roum. Chim., 20 (1975) 259.
3 V. Majer, J. Veselý and K. Stulik, Anal. Lett., 6 (1973) 577.
4 E. Hansen and J. Růžička, Anal. Chim. Acta, 72 (1974) 365.
5 J. Růžička and C. Lamm, Anal. Chim. Acta, 53 (1971) 206.
6 M. Sharp, Anal. Chim. Acta, 59 (1972) 137.
7 J. Růžička and J. Tjell, Anal. Chim. Acta, 49 (1970) 346.
8 J. Růžička and J. Tjell, Anal. Chim. Acta, 51 (1970) 1.
9 S. Lal and G. Christian, Anal. Chim. Acta, 52 (1970) 41.
20 J. Ross and M. Frant, Anal. Chem., 41 (1969) 967.
21 Orion Research Inc. Appl. Bull. No. 11.
22 G. Rechnitz and N. Kenny, Anal. Lett., 3 (1970) 259.
23 W. Selig, Mikrochim. Acta, (1970) 168.
24 R. Heistand and C. Blake, Mikrochim. Acta, (1972) 212.
25 J. Hicks, J. Fleenor and H. Smith, Anal. Chim. Acta, 68 (1974) 480.
26 W. Selig, Mikrochim. Acta, (1974) 663.
27 IUPAC Information Bulletin. Appendices on provisional nomenclature, symbols, units and standards No 43, Recommendation for Nomenclature of Ion-selective Electrodes, Jan. 1975.
28 G. Moody and J. Thomas, Selective Ion Sensitive Electrodes, Merrow, Watford, 1971.
29 Orion Res. Inc. Newslett., 3 (1971) 25.
30 E. Pungor and K. Tóth, Anal. Chim. Acta, 47 (1969) 291.
31 K. Tóth and E. Pungor, Anal. Chim. Acta, 64 (1973) 417.

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CALCIUM-SELECTIVE ELECTRODES WITH PVC MEMBRANES AND SOLID INTERNAL CONTACTS

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SUMMARY

The response of calcium-selective electrodes based on PVC membranes has been investigated. The membrane, containing the calcium salt of di-n-octylphenylphosphoric acid, is in direct contact with the internal electrode made of silver, silver/silver chloride, or teflonized graphite. Evidence is given to support the hypothesis that the oxygen half-cell is responsible for the potential at the solid contact—membrane interface. Silver or teflonized graphite contacts provide better potential stability and analytical sensitivity than Ag/AgCl contacts. The electrodes can be used for determination of calcium in waters.

The constant development of ion-selective electrodes is leading to sensors which not only have better performance but are also of simpler and more reliable construction. Most calcium electrodes are based on the early work of Ross [1] who used calcium didecylphosphate in di-n-octylphenylphosphonate as liquid exchanger. In most later electrodes, only the organic hydrophobic groups are changed; an exception is the linear exchanger used by Ammann et al. [2], which shows good selectivity for divalent cations, in preference to monovalent cations.

An important step was the immobilization of the exchanger in a neutral matrix, of which the PVC membrane [5] shows the best properties. Data concerning such electrodes are collected in Table 1. Most electrodes use a system of internal solution or paste [9] which is well defined electrochemically. In some papers the possibility of using solid contacts to which the membrane adheres has been mentioned and a more detailed study of such systems is described in this paper.

EXPERIMENTAL

Apparatus

Potentials were measured with an Orion 801A digital ionalyzer, coupled with a printer (Orion 751). The reference electrode was an Orion 90-02 double-junction electrode containing 10 % KNO_3 solution.

The pH was measured with an automatic titrator (Radelkis OP-506) used in unbuffered media as a pH-stat.

TABLE 1

Characteristics of the calcium-selective electrodes with immobilized ion-exchanger

Exchanger[a]	Matrix	Internal contact[b]	Linear range pCa	Selectivity coefficient					Ref.
				Na^+	K^+	Mg^{2+}	Ba^{2+}	Zn^{2+}	
Ca-DOP	Collodion	soln.	1—4	0.029	0.034	0.34	0.90	—	3
			1—3.6	0.015		0.12	0.079	—	4
Orion	PVC	soln.	1—4.3	$6.7 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$	0.036 – 0.22	0.005 – 0.013		5
Ca-TDDP	PVC	soln.	1.5—4	0.0028		0.024			6
Ca-DEHP	PVC	soln.	to 4.7	46	14	0.057	0.048		7
DEUTMDA	PVC	soln.	1—7	$3.2 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$3.2 \cdot 10^{-5}$	$4 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	8
Ca-DOPP(I)	PVC	TG	to 5.8	$6.3 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	$2.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	0.06	9
Orion	PVC	Pt	1—5			0.014		32.5	10
Ca-DOPP(II)	PVC	Pt	1.5—4.9	$<10^{-3}$	0.006	0.052	0.038	186.9	11, 12
Orion	PVC	G	1—5			0.009	0.018	0.27	13
Orion	C paste		1—3						14

[a] Ca-DOP = calcium dioctylphosphate. Orion = Orion 92-20-02 exchanger. Ca-TDDP = Monocalcium dihydrogen tetra-(didecylphosphate) and dioctylphenylphosphonate. Ca-DEHP = Calcium bis(di-2-ethylhexylphosphate) in di-n-octylphosphonate. DEUTMDA = *N,N'*-di[(11-ethoxycarbonyl)undecyl]-*N,N'*,4,5-tetramethyl-3,6-dioxaoctane amide in *o*-nitrophenyl-n-octylether with sodium tetraphenylborate. Ca-DOPP(I) = Calcium salt of di-n-octylphenylphosphoric acid and di-n-octylphosphonate. Ca-DOPP(II) = Bis[di(octylphenyl)phosphate]-calcium(II) and di-(2-ethylhexyl I)-2-ethylhexyl phosphonate.

[b] Internal contacts; soln. = solution; G = graphite; TG = Teflonized graphite with calomel paste.

Electrode construction

The electrodes consisted of a body with exchangeable ends. The aim was to keep the PVC membrane close to the solid contact, which was silver, covered or uncovered with AgCl, pressed into a teflon block, or a teflonized graphite layer. Good contact was ensured by a steel spring. In such systems, the exchange of the membrane presents no difficulties.

Membranes with a thickness of 0.15—0.8 mm were prepared as usual [9]. Di-n-octylphenylphosphonate was synthesized as described by Griffiths et al. [6], and calcium di(n-octylphenyl)phosphate as described by Růžička et al. [9]. These compounds were mixed in a 10:1 (weight) ratio for preparation of the exchanger.

RESULTS AND DISCUSSION

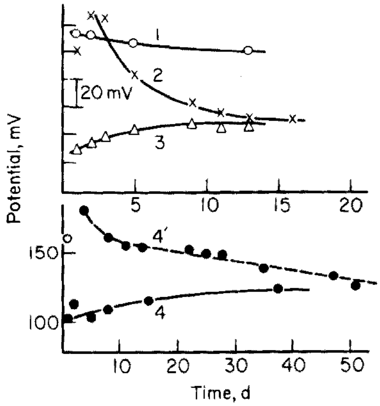
Effect of internal electrode contact

Constant electrode potentials can be obtained only when the internal contact forms a system which is well defined electrochemically and is of reasonable stability. Cattrall et al. [11] suggested that for the coated-wire electrodes, this is provided by the existence of an oxygen half-cell, the necessary gas concentration being obtained by oxygen diffusion through the PVC membrane.

Preliminary experiments with the electronic conductor (graphite, silver, or silver/silver chloride) placed directly in the liquid exchanger supported by a porous wick failed to give constant potentials. The potentials measured on successive days varied by 10—30 mV, although the calibration curves were linear with a slope (22—26 mV/pCa) only slightly smaller than the theoretical one. This suggests that there was no well defined potential at the internal electrode.

Several electrodes were prepared with the same type of PVC membrane (thickness 0.15 mm) containing ion-exchanger, but with different internal contacts. These were Ag, Ag/AgCl and teflonized graphite with and without a paste of the calomel mixture containing calcium sulphate [9]. The electrodes with the silver or teflonized graphite contact are comparable with those containing teflonized graphite and paste (Fig. 1). Significantly worse response was observed for the Ag/AgCl electrode; the potential changed by over 60 mV during the first 10 days. This seems to be justified because the oxygen half-cell may be formed for the silver and contacts, but not for the Ag/AgCl contact. For the Ag/AgCl type of electrode, tests were made to see if conditioning of the electrode in concentrated chloride solution had any effect on the potential stability. No systematic differences were observed for electrodes kept in 1 M calcium chloride or calcium nitrate between measurements (Fig. 2).

If the potential stability of the electrodes with silver or teflonized graphite contacts is due to formation of an oxygen half-cell, the rate of potential change in the initial period of use of the electrode should depend on the



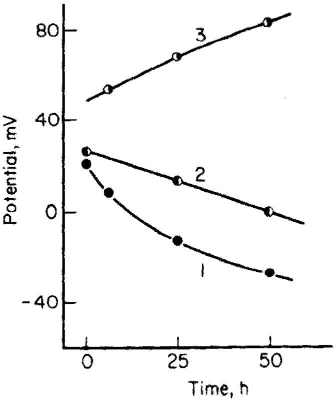


Fig. 1. Changes in the potential of calcium electrodes with various solid contacts for pCa = 4. (1) Ag; (2) Ag/AgCl; (3) teflonized graphite + calomel paste; (4) and (4') teflonized graphite. Membrane thickness: (1, 2, 3, 4) 0.15 mm; (4') 0.5 mm.

Fig. 2. Changes in the potential of calcium electrodes (pCa = 4) with the Ag/AgCl internal solid contact kept in 1 M $CaCl_2$ solution (curve 1) and in 1 M $Ca(NO_3)_2$ solution (curves 2 and 3)

membrane thickness; this effect was in fact observed for 0.15 mm and 0.5 mm PVC membranes. For the thin membrane the potential shift nearly ceased after 10 days, whereas it did not stop for the thick membrane (Fig. 1).

This seems to be confirmed by another experiment. Two identical electrodes with silver contacts were placed in 10^{-3} M calcium(II) solutions. In the air-saturated sample the potential changes during 150 min were less than 20 mV; in a solution deaerated continuously by a stream of argon gas, the potential change was about 70 mV during 150 min (Fig. 3).

Basic electrode characteristics

The electrodes were calibrated at 25 ± 1 °C in the range pCa 3—6 by stepwise addition of calcium chloride solution to distilled water. During 60 days of testing, the slopes of the calibration curves were, in most cases, 29.6 ± 1.0 mV/pCa for the sensors with silver and teflonized graphite contacts. The slope for the electrode with the Ag/AgCl contact was slightly smaller, i.e. 28.4 ± 0.7 mV. For thin membranes, the results were more reproducible, and therefore in further experiments the thickness 0.15 mm was used.

The calibration curve for the silver contact electrodes was linear to pCa 5.5, whereas for TG contacts no curvature was noted until just above pCa 6.0 After one month of electrode use this limit decreased by not more than 0.2—0.3 pCa; after another two months, the changes were insignificant. Some change of electrode sensitivity after several weeks of use was indicated by a decrease in the potential change at the end-point of calcium titrations with EDTA. In titrations of 10^{-3} M calcium(II) in ammonia buffer pH 9, the

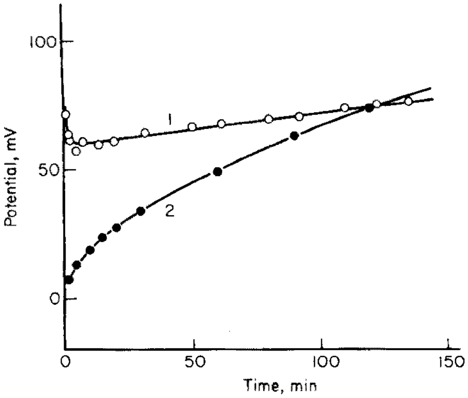


Fig. 3. Changes in the potential of calcium electrodes with Ag internal solid contacts immersed in 10^{-3} M Ca^{2+} solution immediately after mounting of the new membrane. (1) Air-saturated solution. (2) Solution deaerated with argon.

potential jump was 150 mV, which corresponds to an electrode limit of detection of 10^{-8} M. Theoretically, the potential change between $f = 0$ and $f = 2$ should be close to 190 mV, corresponding to a limit of $10^{-9.3}$ M. After 6 weeks, the titration curve was essentially unchanged, but there was some flattening of the curves after the electrode had been used for 6 months. Nevertheless, the potential changes in titrations were significantly larger than those obtained by Cattrall and Drew [12] for the coated-wire calcium-selective electrodes.

Some data on the reproducibility of the electrode potentials were given in the discussion of various types of internal contacts. For the final models of the electrode with the silver or teflonized graphite contacts, the potential shift was not greater than 1 mV d^{-1} after the initial 2—3 days. The standard potentials of electrodes with different internal contacts (Ag, teflonized graphite) approach the value 200 ± 30 mV vs. SCE after several days of electrode use. This is close to the potential given by Cattrall and Drew [12] for the coated-wire electrodes, and also to the value of the internal electrode immersed directly in air-saturated solutions of calcium nitrate. For one electrode in successive calibrations, the potential scatter for a constant concentration was only about ± 0.8 mV even at the pCa 4.0 level.

For 10^{-2} and 10^{-4} M calcium chloride solutions, the electrode response was independent of pH in the range 5—10.5. The selectivity of the electrodes was studied by addition of increasing amounts of calcium to solutions containing constant level of interfering ions. The selectivity coefficients were calculated as $K = a_{Ca^{2+}}/(a_{Me^{n+}})^{2/n}$, where the calcium activity corresponds to a deviation from the linear part of the calibration curve equal to 9 mV [15] (Table 2). The selectivity coefficients are independent of the type of solid contact and do not change for at least 6 weeks after the electrode preparation. For the silver contact electrode, a slight decrease of selectivity was noted after 10 weeks, but in pure calcium(II) solutions its response was unaffected.

TABLE 2

Values of selectivity coefficients (pK) for calcium-selective electrodes with different internal contacts

Interfering ion	Type of internal contact			
	Teflonized graphite	AgCl	Ag	Teflonized graphite + paste
0.01 M Mg^{2+}	3.4	3.3	4.5 (3.7)[a]	3.1 (3.60)[b]
0.5 M Na^+	5.6	5.4	5.8 (4.1)[a]	5.2 (5.20)[b]
1 M K^+	6.2	6.0	6.3 (4.2)[a]	6.0 (5.70)[b]
0.1 M NH_4^+			3.4 (3.4)[a]	

[a] After 10 weeks of electrode use. [b] Data given by Růžička et al. [9].

Determination of calcium in waters

In an earlier procedure for calcium determination [16] with the Orion electrode model 92-20, the Constant Complexation Buffer was used with the addition of acetylacetone for masking magnesium. Because the electrodes with the new exchanger [9] shows better selectivity towards magnesium, it was proved that the composition of the buffer could be simplified and acetylacetone omitted. The results of direct measurements of calcium in tap water in comparison with those obtained by EGTA titration indicate the precision and accuracy that can be expected from the reproducibility and stability of potential values (Table 3).

TABLE 3

Determination of calcium in tap water with Constant Complexation Buffer without acetylacetone

Ca taken (EGTA titn.) mg l^{-1}	Ca found		Error %
	mg l^{-1}	Av.	
43.3	42.5, 42.5, 43.0	42.7	−1.4
77.8	76.5, 76.5, 76.5	76.5	−1.7
80.5	82.8, 84.7, 86.8	84.8	+5.3

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REFERENCES

1 J. W. Ross, Science, 156 (1967) 1378.
2 D. Ammann, E. Pretsch and W. Simon, Anal. Lett., 5 (1972) 843.
3 F. A. Schultz, A. J. Petersen, C. A. Mask and R. P. Buck, Science, 162 (1968) 267.
4 G. A. Rechnitz and T. M. Hseu, Anal. Chem., 41 (1969) 111.
5 G. J. Moody, R. B. Oke and J. D. R. Thomas, Analyst (London), 95 (1970) 910.

6 G. H. Griffiths, G. J. Moody and J. D. R. Thomas, Analyst (London), 97 (1972) 420.
7 A. Craggs, L. Keil, G. J. Moody and J. D. R. Thomas, Talanta, 22 (1975) 907.
8 D. Ammann, M. Güggi, E. Pretsch and W. Simon, Anal. Lett., 8 (1975) 709.
9 J. Růžička, E. H. Hansen and J. Chr. Tjell, Anal. Chim. Acta, 67 (1973) 155.
10 R. W. Cattrall and H. Freiser, Anal. Chem., 43 (1971) 1905.
11 R. W. Cattrall, D. M. Drew and I. C. Hamilton, Anal. Chim. Acta, 76 (1975) 269.
12 R. W. Cattrall and D. M. Drew, Anal. Chim. Acta, 77 (1975) 9.
13 A. Ansaldi and S. I. Epstein, Anal. Chem., 45 (1973) 595.
14 J. P. Sapio, J. F. Colarvotolo and J. M. Bobbitt, Anal. Chim. Acta, 67 (1973) 240.
15 G. J. Moody and J. D. R. Thomas, Selective Ion Sensitive Electrodes, Merrow, Watford, England, 1971.
16 A. Hulanicki and M. Trojanowicz, Anal. Chim. Acta, 68 (1974) 155.

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A COATED WIRE ION-SELECTIVE ELECTRODE FOR THE DETERMINATION OF ZINC(II)

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SUMMARY

The potentiometric determination of zinc in chloride solutions with a coated wire electrode is described. The electroactive membrane contains the chlorozincate(II) salt of Aliquat 336S in poly(vinyl chloride). The electrode shows a useful response over the range 10^{-5} M—10^{-1} M zinc(II) in 3 M total chloride solutions in the pH range 1.5—6. The electrode is more responsive to the divalent tetrachlorozincate(II) than to the monovalent trichlorozincate(II) species. Applications in compleximetric titrations, and to the analysis of zinc oxide and zinc concentrates are reported.

Methods for the determination of zinc can suffer from various interference effects so that tedious prior separations are often necessary [1, 2]. This can be a particular problem in the analysis of minerals and ores.

Recent work on the development of coated wire ion-selective electrodes which are sensitive to halocomplexes of iron(III) [3], mercury(II) [4], and copper(II) [5] suggested that a similar approach would be useful for the determination of zinc. The ion-selective membranes in the earlier electrodes [3—5] consisted of the appropriate halocomplex metal salt of the commercial quaternary ammonium compound Aliquat 336S combined with poly(vinyl chloride). These electrodes were generally found to be more selective towards monovalent halocomplex ions than towards divalent ones.

This paper reports the development of a coated wire ion-selective electrode which is sensitive to the tetrachlorozincate(II) ion, and which can be used, after suitable adjustment of the solution parameters, for the determination of zinc.

EXPERIMENTAL

Materials and equipment

Aliquat 336S (tricaprylylmethylammonium chloride; General Mills Chemical Inc.), poly(vinyl chloride) powder (Monsanto Co.), tetrahydrofuran (May and Baker, reagent grade) and hexane (commercial grade) were used as received. The disodium salt of EDTA (Ajax Chemicals Ltd.), zinc oxide and sodium chloride (B.D.H.) were of analytical-reagent grade, as were all acids used. All other chemicals were of laboratory-reagent grade.

Potentials were measured at room temperature with an Orion Model 801 digital pH meter and a saturated calomel double-junction reference electrode. The outer junction was filled with a saturated potassium chloride solution. Potentials were recorded with a Perkin-Elmer Model 165 recorder. pH was measured with a Radiometer Model 28 pH meter in conjunction with a glass/calomel combined electrode.

Conversion of Aliquat 336S to the chlorozincate(II) form. Scibona et al. [6, 7] studied the extraction of zinc from chloride solutions by long-chain alkylammonium salts dissolved in benzene and found that the highest distribution ratio occurs at a chloride ion concentration of about 3 M in the aqueous phase. The species extracted was suggested to be the tetrachlorozincate(II) ion. In hexane solutions, however, the tetralkylammonium chlorozincate(II) salt precipitates as an insoluble third phase. The procedure used for the preparation of the chlorozincate(II) salt of Aliquat 336S was therefore analogous to that used [4, 5] for the halomercurate(II) and chlorocuprate(II) salts.

An acidic solution (50 cm^3) containing 10^{-1} M zinc and 1 M, 3 M, or 10 M total chloride (0.2 M chloride originating from hydrochloric acid) was shaken with 10 cm^3 of a 0.05 M solution of the chloride form of Aliquat 336S dissolved in n-hexane for about 10 min. A whitish, opaque oil was precipitated as an insoluble third phase. The oil became more opaque and viscous with increasing chloride ion concentration of the aqueous phase. The very viscous oil obtained in the extraction from the 10 M chloride solution was also slightly yellow in color. The oil was separated, repeatedly rinsed with fresh hexane, and then heated on a steam bath to remove excess of solvent.

Construction of electrodes. The oil obtained from each preparation was combined with poly(vinyl chloride) in the ratio of 70 % oil to 30 % PVC (w/w), and the mixture was dissolved in the minimum quantity of tetrahydrofuran. The viscous solution obtained was used to coat a bead formed on the tip of a platinum wire, as described previously [3]. The coating in the case of the oil from the 1 M chloride extraction was white and barely transparent; the transparency decreased with increasing chloride concentration used in the extraction of the oil. The electrodes designated A, B, and C correspond to preparations of the oil obtained by extraction from 1 M, 3 M and 10 M chloride solutions, respectively. The membrane of electrode C was shiny and slightly yellow.

New electrodes were conditioned initially for 3 h in a 10^{-1} M zinc solution containing the same concentration of chloride as was used in the extraction work, and then for 30 min in an acidic chloride solution of the same concentration but without zinc. Electrodes were reconditioned by soaking in the same solutions but for shorter periods of time.

Electrodes of this type should not be rinsed with distilled water because this may necessitate reconditioning in the zinc solution. All rinsing should be done with solutions containing the same chloride concentration as the solutions being tested.

Standard zinc solutions. Zinc solutions (10^{-5} M—10^{-1} M) were prepared as follows. A weighed amount of zinc oxide was dissolved in a small quantity (to produce a final concentration of 0.25 M chloride) of standard 1.0 M hydrochloric acid, and then an appropriate amount of a standard lithium chloride solution (pH about 1.6) was added so that the final solution contained 10^{-1} M zinc and the desired total chloride concentration. Solutions of lower zinc concentration were obtained by successive dilution with the appropriate standard acidified lithium chloride solution.

Procedures

pH Dependence. The effect of the solution pH on the electrode potential was studied by the addition of sodium hydroxide to solutions of zinc oxide dissolved in a mixture of hydrochloric acid and lithium chloride. The effect was also studied in the presence of iron(III). The solution pH and electrode potential were recorded after each addition and after thorough magnetic stirring.

Potentiometric titrations. The pH of the zinc solution in 3 M chloride was initially adjusted to about 2 with sodium hydroxide, and then to pH 5.4 with solid sodium acetate. EDTA solutions in 3 M sodium chloride solution were standardized against a zinc solution to an eriochrome black T end-point [8].

Interference studies. These were carried out by the graphical procedure of Moody and Thomas [9]. The concentration of the interfering ion was generally fixed at 10^{-1} M or 10^{-2} M while the total concentration of zinc was varied between 10^{-5} M and 10^{-1} M. Standard zinc solutions were prepared as described above except that solid sodium chloride was used to adjust the total chloride concentration to 3 M. The interfering ions were added as the solid sodium, potassium, chloride, sulphate, or acetate salts.

Analytical investigations. The zinc content of zinc oxide was determined by titration with EDTA as described above. Certain zinc concentrates were analysed by direct potentiometry; it was important to match the total chloride concentration in the sample and standard solutions closely.

The zinc concentrates (about 0.1 g, dried at 105 °C for 1 h) were dissolved in 10 cm^3 of 11 M hydrochloric acid by allowing to stand for 15 min, and then evaporating gently to about 5 cm^3; 2.5 cm^3 of 14 M nitric acid was added carefully and the solution evaporated to a moist salt. After evaporation (three times) with 2 cm^3 of 11 M hydrochloric acid to remove nitrogen oxides, the solution was evaporated to dryness under a lamp. The residue was dissolved in about 10 cm^3 of 0.1 M hydrochloric acid overnight, filtered if necessary, and made to volume (25 cm^3). The total chloride concentration was determined by potentiometric titration with silver nitrate, and the total chloride concentration was adjusted accurately to 3 M by addition of solid sodium chloride after ten-fold dilution of the sample solution.

Alternatively, the residue was dissolved in a 1.0 M hydrochloric acid—2.0 M sodium chloride solution and made to volume (25 cm^3) with an acidified 3 M sodium chloride solution (pH about 2). This solution was then diluted 20 times with the acidified sodium chloride solution so that the amount of chloride originating from the decomposition process became negligible. The former method was preferred for the analysis of concentrates which contained relatively low amounts of zinc (<10 %).

The pH of the solution was then adjusted to about 4 to precipitate any iron(III) present, by addition of solid sodium acetate (10^{-2} M acetate) and sodium hydroxide.

Triplicate analyses were carried out on each sample and many measurements were made of the potential for each solution.

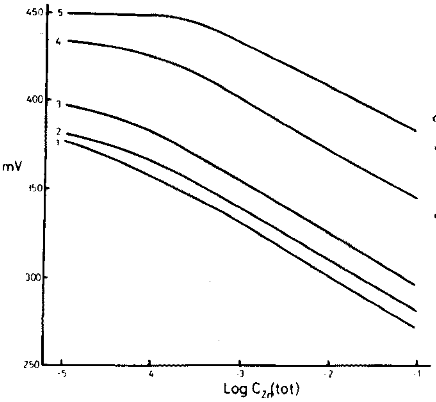
RESULTS AND DISCUSSION

Response characteristics

The response of electrode A in 10^{-5} M—10^{-1} M zinc solutions for various concentrations of total chloride is shown in Fig. 1. The method of preparation of the Aliquat chlorozincate(II) salt has a considerable bearing on the slope of the response curves, the slope decreasing with increase in the total halide concentration used in the preparation. Thus of the three electrodes studied, electrode A, which was prepared with the Aliquat salt extracted from a 1 M total chloride solution, gave the largest change in potential per decade change in zinc concentration. All results presented here therefore refer to electrode A unless stated otherwise.

As with other electrodes of this type [3—5], the slope of the calibration curve indicates that the electrode responds to the anionic chlorozincate(II) species. The increasing magnitude of the potential change between 10^{-5} and 10^{-3} M zinc with increasing total chloride concentration is consistent with the presence of increasing amounts of the anionic chlorozincate(II) species.

The formation constants for the trichlorozincate(II) and tetrachlorozincate(II) species are not particularly large [7], so that these species are not present in high concentrations in the solutions studied. Figure 2 shows the relative concentrations (calculated by the method of Freiser and Fernando [10]) of the chlorozincate(II) species, for a total zinc(II) concentration of 10^{-2} M, as a function of the free chloride concentration. For solutions containing 0.5 M free chloride only about 0.4 % of the zinc is present as anionic species. For 1 M free chloride, the value is only about 2.2 % which demonstrates the sensitivity of the electrode towards anionic chlorozincate(II) species. In this system, the free and total chloride concentrations are almost identical because of the relatively low values for the formation constants of the chlorozincate(II) species. At a very high concentration of free chloride (8 M), the electrode responds almost in a Nerstian manner down to 10^{-5} M total zinc with a change of 28—29 mV per decade change in zinc concentration. This suggests that the electrode is responding



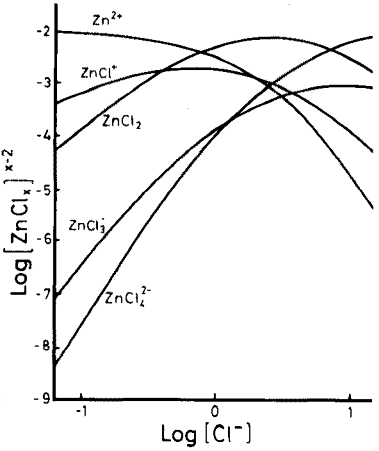


Fig. 1. Response of the chlorozincate(II) electrode. Total chloride: (1) 8 M; (2) 6 M; (3) 3 M; (4) 1 M; (5) 0.5 M.

Fig. 2. The relative concentrations of the chlorozincate(II) complexes as a function of the free chloride concentration for 10^{-2} M total zinc(II).

primarily to the divalent tetrachlorozincate(II) species which is present to the extent of about 50 % of the total zinc concentration in these solutions.

At 1 M total chloride, the concentrations of the trichlorozincate(II) and tetrachlorozincate(II) species are quite similar, but the potential change per decade change in zinc concentration is still only about 28 mV in the regions 10^{-2}—10^{-1} M and 10^{-3}—10^{-2} M total zinc. If the electrode responded preferentially to the monovalent anionic complex, as was found with the mercury(II) electrode [4], the potential difference in these regions would be much larger, which suggests that the chlorozincate(II) electrode is more selective towards the divalent anion than the monovalent one. The differences between the zinc(II) and mercury(II) electrodes might be elucidated by a detailed study of the extraction systems with Aliquat 336S.

The response time of the electrode was short. About 5 min was required to reach a stable potential (±0.1 mV) in 10^{-5} M total zinc solutions containing 3 M chloride; the response was instantaneous in 10^{-1} solutions. Reproducibility of the potentials from run to run was within 1 mV at zinc concentrations above 10^{-4}.

The long-term reproducibility of the calibration graphs was studied during 8 days by storing the electrode (a) dry in air and (b) in a 3 M acidic chloride solution, when not in use. When the electrode was stored in air, and then conditioned in the usual way, the response gradient remained within 1 mV of the original value, but the absolute potential decreased by 10 mV over the 8-day period. When the electrode was stored in a 3 M acid chloride solution, the response gradient decreased gradually at zinc concentrations below 10^{-3} M, and the absolute potential decreased by about 14 mV over the 8-days. In this case, the electrode characteristics could be restored by drying the electrode in air and reconditioning.

Chloride ion and pH dependence

The potential response of the electrode was measured as a function of the total chloride concentration for 10^{-1} M zinc solutions. The potential decreased systematically with increasing concentration of chloride, because of the increased concentration of tetrachlorozincate(II). The behaviour was in marked contrast to that for the analogous mercury(II) system [4] where a minimum and then a plateau region in the graph of potential against chloride concentration was observed. The result for the zinc electrode supports the suggestion that the electrode is more selective towards the tetrachlorozincate(II) species.

The graphs of electrode potential against solution pH are shown in Fig. 3. For a solution containing 10^{-2} M total zinc and 3 M total chloride, the potential was independent of pH below 7. Above pH 7, zinc precipitated; the pH of precipitation varied slightly with the total zinc and total chloride concentrations, being higher for high chloride and low zinc concentrations.

In the presence of 10^{-3} M iron(III), which interfered strongly, a second plateau region occurred, because of the effect of tetrachloroferrate(III) on the electrode. However, precipitation of the iron(III) was complete at about pH 3.7, and the electrode then responded only to the tetrachlorozincate(II) ion.

Interference studies

The interference of numerous ions was studied in acidic solutions. The interference curves for the most strongly interfering ions are shown in Fig. 4 where the relative potential is plotted against the logarithm of the total zinc concentration for a constant concentration of the interfering ion. Relative potential values are used for convenience to allow each curve to be

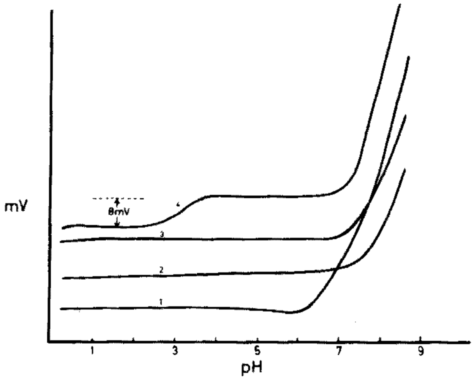


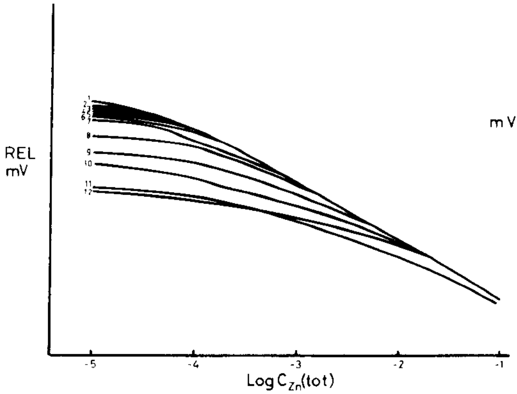
Fig. 3. pH dependence of the chlorozincate(II) electrode (1) 10^{-1} M Zn(II), 3 M Cl^-. (2) 10^{-2} M Zn(II), 6 M Cl^-. (3) 10^{-2} M Zn(II), 3 M Cl^{-1}. (4) 10^{-2} M Zn(II), 10^{-3} M Fe(III), 3 M Cl^-. (Note: the curves have been separated for clarity).

shown relative to a single standard curve for pure zinc solutions. The order of increasing interference for the strongly interfering cations is $Cu^{2+} < Cd^{2+} < Fe^{3+} < Hg^{2+}$ with, of course, Ag^+ and Pb^{2+} precipitating as the insoluble chlorides. The high interference of Fe^{3+} and Hg^{2+} is expected in view of previous work [3, 4]. Other cations, Ca^{2+}, Mg^{2+}, Al^{3+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Co^{2+}, Fe^{2+} and Ba^{2+} showed negligible interference. Acidic solutions were used in order to observe the interference effects of foreign cations, but the selecitivity of the electrode can be improved by working at higher pH values (e.g. pH 5) under which conditions many potentially interfering ions will be precipitated. This is demonstrated by curves 5 and 11 in Fig. 4 where adjustment to pH 4.5 leads to precipitation of most of the iron (III), and the removal of that ion as a series interferent.

Figure 4 shows that the order of increasing interference for the common anions is $Br^- < NO_3^- < I^- < ClO_4^-$; the only really serious interferent was perchlorate. Other anions studied, SO_4^{2-}, CH_3COO^-, F^- and $H_2PO_4^-$ (10^{-2} M) showed negligible interference.

Potentiometric titrations

Four curves are shown in Fig. 5 for the potentiometric titration of chlorozincate(II) solutions with EDTA. The method relies on the relatively large change in potential associated with the decrease in the concentration of the



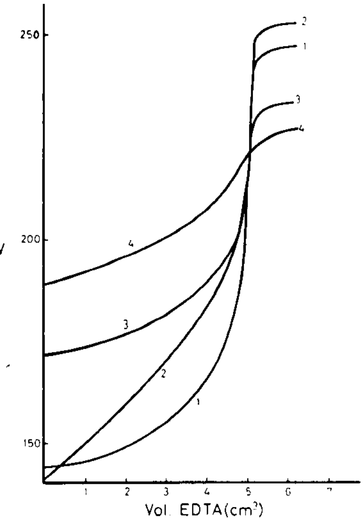


Fig. 4. Interference curves for the chlorozincate(II) electrode. (1) Pure solutions. (2) 10^{-2} M Co^{2+}. (3) 10^{-2} M NO_3^-. (4) 10^{-1} M Br^-, 10^{-3} M I^-. (5) 10^{-2} M Ba^{2+}, 10^{-2} M Fe^{2+}. (6) 10^{-3} M Fe^{3+} (pH 4.5). (7) 10^{-2} M Cu^{2+}. (8) 10^{-1} M NO_3^-. (9) 10^{-2} M I^-. (10) 10^{-4} M Hg^{2+}. (11) 10^{-3} M Fe^{3+} (pH < 2). (12) 10^{-3} M ClO_4^-.

Fig. 5. Titration of chlorozincate(II) solutions with EDTA (1) 5 cm³ of $5 \cdot 10^{-2}$ M Zn^{2+}, 3 M Cl^- against $5 \cdot 10^{-2}$ M EDTA, 3 M Cl^-. (2) 5 cm³ of $5 \cdot 10^{-2}$ M Zn^{2+}, 3 M Cl^- against $5 \cdot 10^{-2}$ M EDTA. (3) 5 cm³ of $5 \cdot 10^{-3}$ M Zn^{2+}, 3 M Cl^- against $5 \cdot 10^{-3}$ M EDTA, 3 M Cl^-. (4) 5 cm³ of $5 \cdot 10^{-4}$ M Zn^{2+}, 3 M Cl^- against $5 \cdot 10^{-4}$ M EDTA, 3 M Cl^-.

chlorozincate(II) species on complexation of zinc with EDTA. The curves show that quite low concentrations of zinc can be titrated. Figure 5 also shows that better inflections are obtained in the titration curves if the EDTA initially contains 3 M chloride, otherwise the dilution of the total chloride in the zinc solutions leads to a decrease in the concentration of the chlorozincate(II) species (compare curves 1 and 2).

Analytical investigations

The results of the analysis of a sample of zinc oxide and four zinc concentrates are shown in Table 1. There is reasonable agreement between the values obtained by the chlorozincate(II) electrode and the known values. The results suggest that ion-selective potentiometry with the chlorozincate(II) electrode is a promising technique for the analysis of zinc ores and concentrates. If direct potentiometry is used, the total chloride concentration in the sample and standard solutions must be controlled very closely. However, this careful control is unnecessary for potentiometric titrations.

TABLE 1

Analysis of zinc concentrates by direct potentiometry, and zinc oxide by potentiometric titration

(Unless otherwise indicated, uncertainties are expressed as $\pm 2\sigma$ where σ is the standard deviation determined for n potential measurements of each triplicate series; n is shown in parenthesis.)

Sample	Source	Other elements	Zn % present	Zn % found
MIM Zn3	Flotation[a] product	—	9.9, 10.8, 10.0[a]	10.09 ± 0.48(8)
MP-1	NBS SRM	Sn, Cu, Pb, Mo, In, Bi, As, Ag	16.33[b]	16.39 ± 1.50(33)
113a	NBS SRM	Pb, Fe, Ca, Mg, Cd, Cu, Co, Ni, S, Si, Ag	57.3[b]	57.65 ± 2.85(23)
SAS 41G	BAS, Ltd	Fe, Pb, Cu, As, Mn, Cd, Ca, S, F	52.5[b]	50.85 ± 2.94(27)[c]
ZnO	B.D.H. (A.R.)	—	80.15 ± 0.05[d,e]	79.9 ± 0.1[e]

[a] Ref. [11]. [b] Certified value. [c] This value may be affected by the relatively large amount of iron (8 %) in the sample. [d] Compleximetric titration [8]. [e] Mean deviation from three determinations.

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REFERENCES

1 R. S. Young, Chemical Analysis in Extractive Metallurgy, Griffin, London, 1971.
2 I. M. Kolthoff and P. J. Elving, Treatise on Analytical Chemistry, Part II, Analytical Chemistry of the Elements, Vol. 3, Interscience, New York, 1961, p. 98.
3 R. W. Cattrall and Chin-Poh Pui, Anal. Chem., 47 (1975) 93; Anal. Chim. Acta, 78 (1975) 463.
4 R. W. Cattrall and Chin-Poh Pui, Anal. Chem., 48 (1976) 552.
5 R. W. Cattrall and Chin-Poh Pui, Anal. Chim. Acta, 83 (1976) 355.
6 G. Scibona, L. Mantella and P. R. Danesi, Anal. Chem., 42 (1970) 844.
7 G. Scibona, F. Orlandini and P. R. Danesi, J. Inorg. Nucl. Chem., 28 (1966) 1313.
8 A. I. Vogel, A Text-Book of Quantitative Inorganic Analysis, 3rd edn., Longmans, London, 1961, p. 433.
9 G. J. Moody and J. D. R. Thomas, Talanta, 19 (1972) 623.
10 H. Freiser and Q. Fernando, Ionic Equilibria in Analytical Chemistry, John Wiley, New York, 1963, Ch. 9.
11 B. J. Heffernan, Third Australian Symposium on Analytical Chemistry, Melbourne 1975, paper W14.

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THE DETERMINATION OF CYANIDES IN STEELWORKS EFFLUENTS WITH A CYANIDE-SELECTIVE ELECTRODE

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SUMMARY

Conventional methods for the determination of cyanide in effluents associated with steel-making procedures are compared with a method based on a cyanide-selective electrode. For cyanide levels above 1.0 mg l^{-1}, the standard argentimetric titration and electrode method give similar results. At lower levels (0.1—1.0 mg l^{-1} and 0.01—0.10 mg l^{-1}), the potentiometric method is compared with pyridine—pyrazolone and pyridine—barbituric acid colorimetric procedures; the pyrazolone method tends to give higher results than the other two methods. Synthetic standards and actual effluent samples are discussed. Problems associated with the determination of cyanide in effluents containing complex iron cyanides and sulphides are examined. Sulphide removal with lead carbonate or cadmium carbonate above pH 11 should not be done until after the distillation.

Waste waters from processing installations associated with steelmaking often contain free cyanides and complex iron cyanides such as semi-colloidal Prussian blue or Turnbull's blue. Most methods of determining total cyanide in effluents employ titrimetric or colorimetric procedures [1, 2], all of which involve a preliminary reflux distillation under vacuum to separate the cyanide from interfering substances and to break down complex cyanides. Many of the colorimetric procedures are based on the König synthesis for pyridine dyestuffs, in which cyanogen bromide or chloride reacts with an aromatic amine, such as benzidine, pyrazolone/bis-pyrazolone and barbituric acid.

A cyanide-selective membrane electrode can be used to determine cyanides as an alternative to the above procedures. The cyanide electrode has a silver iodide—silver sulphide membrane [3], and in alkaline solution (pH 12) the exchange reaction

$$AgI + 2\,CN^- \rightleftharpoons Ag(CN)_2 + I^- \qquad (1)$$

occurs at the surface of the membrane. The cyanide activity in solution is related to the potential by

$$E = E_0 - k \log a \qquad (2)$$

where the terms have their usual meaning. At low concentrations in solutions of constant ionic strength, the measuring system determines the concentration of free cyanide. The most likely interference is sulphide which is distilled over as hydrogen sulphide together with hydrogen cyanide. It is recommended that sulphide be removed before the distillation by addition of lead carbonate or cadmium carbonate at pH > 11 [1, 2]. However, in the presence of partially soluble complex metal cyanides such as Prussian blue and Turnbull's blue, the removal of sulphide before the distillation may also remove these complexes. To obtain a more precise measurement of total cyanide, sulphide should be removed after the distillation. The possibility of complex formation of cyanide with zinc or cadmium must also be considered.

Cyanide has been determined in synthetic standards and almond distillates, and the electrode method has been shown [4] to be more precise than the argentimetric titration. Other workers have measured cyanide in various plants and brandies [5]. Continuous monitoring of cyanide under flow stream conditions has been reported for the range 10^{-2}—$5 \cdot 10^{-5}$ M cyanide [6].

Other studies have been concerned with the determination of cyanide in the presence of complex-forming metal ions, such as cadmium, zinc, nickel, chromium, mercury and copper [4, 6—8].

In this laboratory, cyanides are determined after a preliminary distillation under acidic conditions by titrimetric, colorimetric or electrometric methods. The choice is dictated by the concentration of cyanide. These methods were compared for synthetic cyanide solutions and actual steelworks waste waters, in three concentration ranges from > 1.0 mg CN l^{-1} to 0.01 mg l^{-1}.

EXPERIMENTAL

Apparatus

All distillations were done in Quickfit assemblies. A 500-ml round-bottom flask (FB 500/3 M) was fitted with a multiple adapter (MA 1/3) which carried a funnel (D 1/22) and a condenser (C 5/22); the condenser was attached by a stillhead (ST 5/2) to flexible tubing leading to a 50-ml test-tube absorber, the outlet tube from which was attached to a water pump. Six identical assemblies were placed on a multiple electrothermal heating mantle so that analyses could be done concurrently. The distillation time was 2 h. For effluents a 100-ml sample volume was used. The liberated hydrogen cyanide was absorbed in 25 ml of 1M sodium hydroxide and subsequently transferred to a 100-ml volumetric flask.

A Beckman DU4700 spectrophotometer was used for all colorimetric determinations. The procedures for the pyrazolone and barbituric acid methods were essentially the same as those quoted in standard references [1, 2].

Electrometric measurements were made with a Corning-EEL model 110 expanded scale pH meter, an Orion model 94-06 cyanide electrode and an Orion model 90-01 single-junction reference electrode. All solutions were stirred magnetically at constant rate with a 30-mm teflon-coated bar. The cyanide electrode was rinsed clean and stored dry when not in use.

Reagents

A stock solution (1.000 g CN l^{-1}) was prepared by dissolving 2.0 g potassium hydroxide and 2.51 g potassium cyanide in 1 l of distilled water. This solution was used for preparation of standards in the colorimetric and electrometric determinations. For the titrimetric determinations, a 0.0192 M silver nitrate solution was standardized against 0.0192 M sodium chloride solution using a 5.00-ml microburrette.

All the chemicals used were analytical-reagent grade.

Calibration of electrodes

Standard cyanide solutions of constant ionic strength (0.25 M sodium hydroxide) covering the range 0.01—100.0 mg CN l^{-1} were prepared. The electrodes were calibrated daily. The calibration graphs showed a Nernstian response for cyanide activities of 0.1—100 mg l^{-1}, with slight curvature in the range 0.01—0.1 mg l^{-1}. For cyanide levels below 0.1 mg l^{-1}, an equilibration time of 10 min was allowed. Before calibration, the electrodes were placed in 0.25 M sodium hydroxide solution until the meter stabilized

RESULTS AND DISCUSSION

Comparison of methods

The methods were compared at three levels of cyanide (Table 1). For the highest level (>1 mg l^{-1}), argentimetric titration was compared with the ion-selective electrode method. Samples A—F were taken from a coke oven breeze basin which had been receiving weak ammonia liquor as make-up. For the intermediate level (0.1—1.0 mg l^{-1}), treated waters from a treatment plant for blast furnace effluents were chosen (samples G—L). In the low range (0.01—0.10 mg l^{-1}), samples M—R were taken from a mill recirculated cooling water system. Generally, the results (Table 1) show a close agreement between the electrometric and other methods at all levels. At the lowest level (<0.1 mg l^{-1}), there is closer agreement to the barbituric acid method, while the values obtained with pyrazolone tend to be higher.

This excercise was repeated for the intermediate and low level range for standard solutions taken through the distillation procedure. The results (Table 2) again show good general agreement between the three methods with better correspondence between the electrometric and barbituric acid methods.

To test the reproducibility of the methods, waste waters from a blast furnace water treatment plant and from a mill recirculated water system were analysed six times. The results are shown in Table 3.

TABLE 1

Comparison of results for cyanide determinations (All results are given as mg l^{-1}.)

Sample	Titrimetric	Colorimetric		Electrometric
		Pyrazolone	Barbituric acid	
A	18.6			18.3
B	10.5			10.9
C	13.2			14.1
D	18.4			18.2
E	11.7			11.2
F	5.4			5.1
G		0.35	0.47	0.46
H		0.58	0.52	0.66
I		0.46	0.38	0.30
J		0.62	0.87	0.94
K		0.76	0.72	0.87
L		0.68	0.42	0.46
M		0.05	0.04	0.06
N		0.04	0.05	0.07
O		0.14	0.03	0.02
P		0.13	0.07	0.06
Q		0.11	0.04	0.04
R		0.26	0.16	0.10

TABLE 2

Comparison of methods for standard cyanide solutions after distillation (All results are given as mg l^{-1}.)

Nominal concn.	Colorimetric		Electrometric
	Pyrazolone	Barbituric acid	
0.01	0.02	0.01	0.01
0.03	0.03	0.02	0.03
0.05	0.04	0.04	0.05
0.07	0.08	0.06	0.07
0.09	0.02	0.08	0.09
0.11	0.03	0.11	0.10
0.10	0.15	0.12	0.10
0.30	0.30	0.31	0.30
0.50	0.41	0.48	0.52
0.70	0.49	0.68	0.70
0.90	1.11	0.89	0.92

Effect of complex iron cyanides and sulphides

Water from the Hunter River estuary was used; this had previously been analysed and found to contain <0.01 mg CN l^{-1}. Additions of standard solutions were made to 100-ml portions of the water; 10 ml of $6.43 \cdot 10^{-4}$ M potassium hexacyanoferrate(III) containing 1.0 mg CN^-, and 10.0 ml of

TABLE 3

Precision of the methods (Results are given as mg l^{-1}. Each result is the average of 6 determinations.)

	Colorimetric		Electrometric
	Pyrazolone	Barbituric acid	
Blast furnace water			
Average	0.66	0.59	0.75
s	0.11	0.06	0.06
Mills system water			
Average	0.06	0.05	0.05
s	0.03	0.02	0.01

TABLE 4

Determination of cyanide (in mg l^{-1}) in the presence of complex iron cyanides and sulphide

Sample	Titrimetric	Electrometric
	—	<0.01
River water + $K_3Fe(CN)_6$[a]	9.7	9.1
River water + $Fe_3[Fe(CN)_6]_2$[b]	9.7	9.1
River water + $Fe_3[Fe(CN)_6]_2$ + sulphide[c]	4.1	4.2
River water + $Fe_3[Fe(CN)_6]_2$ + sulphide[d]	10.1	9.6

[a] Average of six determinations. [b] Average of five determinations. [c] Single determination; S^{2-} removed before distillation. [d] Average of four determinations; S^{2-} removed after distillation

$1.79 \cdot 10^{-3}$ M iron(II) sulphate heptahydrate containing 1.0 mg Fe^{2+} were added to the river water and allowed to stand for 10 min. Then 2.0 ml of $3.2 \cdot 10^{-3}$ M sodium sulphide solution containing 0.2 mg S^{2-} were added.

The tests were carried out with river water, and potassium hexacyanoferrate(III) or Prussian blue or Prussian blue—sodium sulphide. In the last case, sulphide was removed before or after the distillation. Results by the argentimetric and electrometric methods are compared in Table 4. The recovery of cyanide in the distillation was high and there was good agreement between the two sets of analyses. The low result obtained when sulphide was removed before the distillation suggests that some iron cyanide complex was removed in the filtration step because of entrainment with the precipitate when the solution was made alkaline. As a general rule, sulphide should be removed after the distillation as this gives a more accurate measure of the total cyanide present in effluents.

Absorption of cyanide on cadmium carbonate and lead carbonate

If the removal of sulphide is undertaken after the distillation, cyanide may form complexes with Pb^{2+} and Cd^{2+} or may be lost by occlusion in the precipitated material. To examine this possibility, additions of 0.1 g of cadmium carbonate or lead carbonate were made to a series of standard (5.0 mg l^{-1}) cyanide solutions in 0.25 M sodium hydroxide solution. All determinations were made with the cyanide-selective electrode; a calibration graph for a series of standards containing 0—10.0 mg CN l^{-1} was prepared. The solutions were shaken to disperse the reagents, and the cyanide activities were measured at intervals over a period of 5 h. The concentrations, measured from the original calibration graph, are recorded in Table 5. There was no apparent decrease in the concentration of cyanide caused by complexation; any discrepancies were within the normal experimental errors of the measuring system. In routine analysis of waste waters, the filtration of the prepared solution after distillation and addition of lead carbonate or cadmium carbonate should not be necessary.

CONCLUSIONS

The above evidence suggests that filtration of effluent samples before distillation may remove partially soluble complex iron cyanides. Sulphides may be conveniently removed after the distillation with no adverse effect on the cyanide determination by standard procedures.

The determination of cyanides with a cyanide-selective electrode gives results comparable to those by standard methods. The method should gain wider use as it is simple and requires less analytical expertise than the classical methods. The analysis time is approximately the same as that of the spectrophotometric methods, but there is no need to prepare and store reagent solutions.

For cyanides at levels above 1 mg l^{-1}, argentimetric titration should suffice as it is quite rapid. The effective analytical life of a cyanide-selective electrode is prolonged if it is used only in solutions of very low cyanide concentration [9].

TABLE 5

Determination of cyanide (in mg l^{-1}) in the presence of $PbCO_3$ and $CdCO_3$

Cyanide taken	Cyanide measured after					
	0 h	1 h	2 h	3 h	4 h	5 h
5 mg l^{-1}	5.0	5.1	4.9	4.9	5.0	5.0
5 mg l^{-1} + 0.1 g $CdCO_3$	4.9	4.9	4.7	5.1	5.0	5.0
5 mg l^{-1} + 0.1 g $PbCO_3$	5.0	5.3	4.8	4.9	4.9	5.0

Appreciation is expressed to The Broken Hill Proprietary Company Limited for permission to publish this work.

REFERENCES

1 American Public Health Association. American Water Works Association and Water Pollution Control Federation, Standard Methods for the Examination of Water and Wastewater, 13th edn., New York, 1971.
2 ASTM Designation D2036-74, Part 31.
3 R. A. Durst (Ed.), Ion Selective Electrodes, National Bureau of Standards Special Publication 314, (1969).
4 E. Pungor and K. Toth, Anal. Chim. Acta, 51 (1970) 221.
5 T. S. Light and J. L. Schwartz, Anal. Lett., 1 (1968) 825.
6 B. Fleet and H. Von Storp, Anal. Chem., 43 (1971) 1575.
7 M. Mascini and A. Napoli, Anal. Chem., 46 (1974) 447.
8 M. S. Frant, J. W. Ross and J. H. Riseman, Anal. Chem., 44 (1972) 2227.
9 Instruction Manual, Cyanide Activity Electrode Model 94-06, Orion Research Incorporated, Cambridge, Massachusetts, (1974).

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DETERMINATION OF SELENIUM(IV) IN ACIDIC SOLUTIONS WITH A.C. POLAROGRAPHY AND DIFFERENTIAL PULSE POLAROGRAPHY

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SUMMARY

Selenium(IV) at trace levels can be determined in hydrochloric and perchloric acid solutions by alternating current and differential pulse polarography. The use of a hanging mercury drop electrode with accumulation of elemental selenium followed by cathodic stripping gives detection limits in the range 0.1—1 p.p.b. With a dropping mercury electrode the detection limit is 8 p.p.b. The possible interferences of Te(IV), Ge(IV), Cu(II), Cd(II) and Pb(II) are discussed. The serious interference of lead(II) can be prevented by addition of EDTA.

Selenium is widely employed in the semiconductor industry, in special alloys, and in the production of photosensitive elements, inks, etc. [1]. Nevertheless, it is highly toxic despite its essential biological rôle [2]. The permissible intake level has been estimated to lie generally in the range of some $\mu g\ g^{-1}$ of feed [3]. The recognition of the semiconductor properties and biological importance of selenium have stimulated the development of new sensitive and selective methods for the determination of this element at trace levels. Atomic absorption spectrometry [4—7], spectrophotometry with reagents such as 3,3'-diaminobenzidine [8—10], 2,3-diaminonaphthalene [11, 12] and dithizone [13], x-ray fluorescence [14, 15] and neutron activation analysis [1, 16] have been proposed. The recent text of Nazarenko and Ermakov [1] is valuable in giving comparative data on these methods, but there are few procedures which provide reproducibility and sensitivity down to the p.p.b. level for selenium.

Electroanalytical methods, especially the modern polarographic techniques, allow detection limits of about 10 p.p.b. to be achieved. The early work of Schwaer and Suchy [17] and later work by Lingane and Niedrach [18] showed that Se(IV) is reduced successively to selenium and then to Se^{2-}. The form adsorbed at the surface of the dropping mercury electrode has been discussed [18, 19]; elemental selenium forms a deposit, the transformation of which to Se^{2-} in acidic solutions is accompanied by a strong maximum in classical polarography [20]. In acidic medium, e.g.

1 M HCl or 1 M $HClO_4$, the reduction of $Se^0 \rightarrow Se^{2-}$ occurs at −0.45 V vs. SCE. A sharp, intense peak is obtained in alternating current polarography (a.c.p.) and differential pulse polarography (d.p.p.); this peak is particularly recommended for the determination of selenium in acidic solutions.

In this paper, the possibilities of determining selenium in hydrochloric or perchloric acid solutions in the presence of foreign elements such as Te(IV), Ge(IV), Cu(II), Cd(II) and Pb(II), are discussed.

EXPERIMENTAL

Instrumentation and reagents

A Solea-Tacussel PRG 3 and PRG 4 assembly with a three-electrode circuit was used. All potentials were measured with respect to the saturated calomel electrode (SCE). A platinum wire was used as auxiliary electrode. The characteristics of the dropping mercury electrode (DME) were as follows: 8-s drop time for a mercury height of 50 cm (open circuit); flow rate, 0.3—0.4 mg s^{-1}. An MPO 3 hammer drop timer, and a E 410 Metrohm HMDE were used. All capillaries were treated with dimethyldichlorosilane (5 %) in carbon tetrachloride, to form a thin internal film which prevented rupture of the mercury column. The glass cell was thermostated at 25 ± 0.1 °C.

All solutions were prepared from analytical-grade products (Merck or Prolabo "suprapur"). Water was deionized with mixed ion exchangers and then twice-distilled. The nitrogen used to remove oxygen, was previously passed through 18 M sulfuric acid and then through twice-distilled water. The mercury used had been distilled 6 times (Rhone Alpes Mercure), and was conditioned under nitrogen. The supporting electrolyte was 1 M HCl, 1 M $HClO_4$, or 0.1 M $HClO_4$—0.1 M $NaClO_4$.

Stock solutions (10^{-2} M) of selenium(IV) were prepared by dissolving a measured quantity of selenium dioxide in water, and were stored in polyethylene bottles. Working solutions were made by suitable dilution. Tellurium and germanium dioxides were dissolved in the minimum quantity of sodium hydroxide and the solutions diluted with water to give the required concentrations. Aqueous solutions of copper, cadmium and lead salts were prepared. A 10-μl Eppendorf micropipette was used for all additions.

Procedure

The supporting electrolyte (20 ml) was transferred to the thermostated cell, and oxygen was removed by passing nitrogen for 30 min. Then the blank polarographic curve was measured. Calibration curves were obtained by successive additions of 10-μl aliquots of 10^{-5} or 10^{-4} M selenium(IV) solutions. In the studies of interfering elements like Te(IV), Cd(II), Ge(IV), Cu(II) and Pb(II), the initial solutions in the absence of selenium(IV) were also prepared in the appropriate supporting electrolytes.

When the HMDE (radius, 0.57 mm; area, 4.11 mm^2) was used, a new drop was formed for each voltammogram; an intermediate drop was removed each time to avoid memory effects. Magnetic stirring was done during the preelectrolysis at —0.3 V vs. SCE, and then a period of 30 s elapsed before the voltammograms were recorded. All the precautions usual in polarography were taken.

RESULTS AND DISCUSSION

The optimum experimental conditions for the determination of selenium at trace levels in acidic solutions by a.c.p. and d.p.p. were studied first, and then the effects of some possible interfering elements were examined.

The detection limits obtained for selenium are shown in Table 1. The detection limit was taken as the concentration for which the peak had a measurable width and the peak potential could be determined accurately. Some examples are shown in Fig. 1. The current—concentration plots were always linear over at least two orders of magnitude above the detection limit (Fig. 2). The slopes of the log—log plots are quite close to unity except for curve 6. Curve 6 was obtained by d.p.p. at the HMDE; the linear relationship has a slope greater than unity, and this was verified in several runs.

The detection limits for selenium(IV) were examined in the presence of one interfering element and then in the presence of several elements at a time. Like selenium(IV), tellurium(IV) is reduced in two steps; first Te(IV) gives Te at about —0.2 V vs. SCE, and then the adsorbed elemental tellurium is reduced to Te^{2-} at about —0.7 V vs. SCE, giving an intense peak in a.c.p. and in d.p.p. [21, 22]. There is no significant interference as the peak potential of selenium is situated at —0.5 V vs. SCE. The detection limits are decreased slightly because of the adsorbed tellurium but lie in the range 10—20 p.p.b. depending on the medium chosen (Table 2).

TABLE 1

Detection limits for selenium in acidic media
Preelectrolysis time: [a] 3 min; [b] 2 min; [c] 12 min, at —0.3 V vs. SCE.

Medium	A.c.p.		D.p.p.	
	DME	HMDE	DME	HMDE
1 M HCl	$2.5 \cdot 10^{-7}$ M 20 p.p.b.	$2 \cdot 10^{-9}$ M[a] 0.16 p.p.b.	$2.5 \cdot 10^{-8}$ M 2 p.p.b.	$2 \cdot 10^{-9}$ M[a] 0.16 p.p.b.
1 M $HClO_4$	$2.5 \cdot 10^{-7}$ M 20 p.p.b.	$2 \cdot 10^{-8}$ M[b] 1.6 p.p.b.	$1 \cdot 10^{-7}$ M 8 p.p.b.	$1 \cdot 10^{-8}$ M[b] 0.8 p.p.b.
0.1 M $HClO_4$ 0.1 M $NaClO_4$	$1 \cdot 10^{-7}$ M 8 p.p.b.	$1 \cdot 10^{-9}$ M[c] 0.08 p.p.b.	$1 \cdot 10^{-7}$ M 8 p.p.b.	$1 \cdot 10^{-9}$ M[c] 0.08 p.p.b.

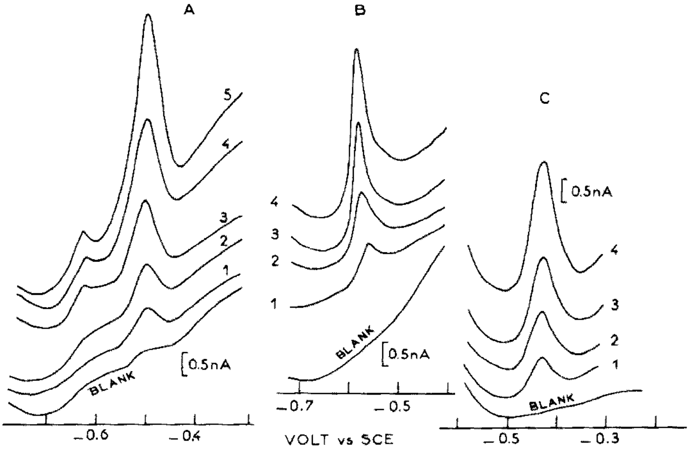


Fig. 1. Polarographic peaks for selenium: (A) In 0.1 M $HClO_4$—0.1 M $NaClO_4$ with a.c.p. and HMDE. Curve (1) 1; (2) 2; (3) 3; (4) 5; and (5) $10 \cdot 10^{-9}$ M.(B) In 0.1 M $HClO_4$—0.1 M $NaClO_4$ with a.c.p. and HMDE in presence of 10^{-5} M Cu(II). Curve (1) 1; (2) 2; (3) 4; (4) $6 \cdot 10^{-8}$ M. (C) In 1 M $HClO_4$ with d.p.p. and DME in presence of 10^{-5} M Cu(II). Curve (1) 1; (2) 2; (3) 2.9; (4) $5 \cdot 10^{-7}$ M.

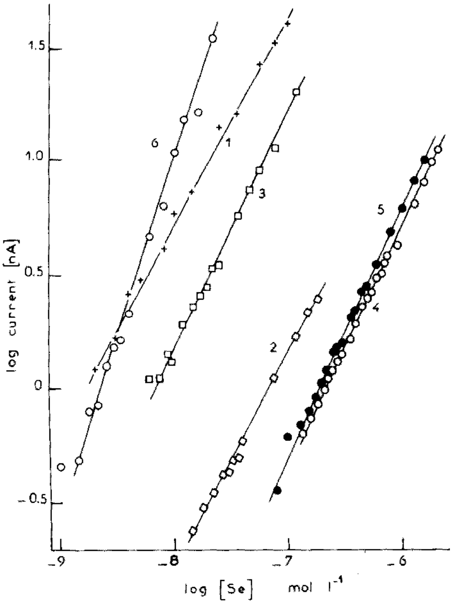


Fig. 2. Some calibration curves for selenium in different media. (1) 1 M HCl, d.p.p. and HMDE. (2) 1 M $HClO_4$, a.c.p. and HMDE. (3) 1 M $HClO_4$, d.p.p. and HMDE. (4) 0.1 M $HClO_4$—0.1 M $NaClO_4$, a.c.p. and DME. (5) 0.1 M $HClO_4$—0.1 M $NaClO_4$, d.p.p. and DME.(6) 0.1 M $HClO_4$—0.1 M $NaClO_4$, d.p.p. and HMDE.

TABLE 2

Detection limits for selenium in presence of tellurium, copper, cadmium and lead, in acidic medium
[a]Preelectrolysis time: 3 min at —0.3 V/SCE.

Medium	Method	Detection limit
1 M HCl, 10^{-5} M Te(IV)	D.p.p. DME	$1 \cdot 10^{-7}$ M (8 p.p.b.)
1 M $HClO_4$, 10^{-5} M Te(IV)	D.p.p. DME	$4 \cdot 10^{-7}$ M (32 p.p.b.)
1 M $HClO_4$, 10^{-6} M Te(IV)	D.p.p. DME	$1 \cdot 10^{-7}$ M (8 p.p.b.)
0.1 M $HClO_4$—0.1 M $NaClO_4$, 10^{-5} M Te(IV)	A.c. HMDE[a]	$1 \cdot 10^{-7}$ M (8 p.p.b.)
	D.p.p. DME	$2 \cdot 10^{-7}$ M (16 p.p.b.)
	D.p.p. HMDE[a]	$2 \cdot 10^{-7}$ M (16 p.p.b.)
0.1 M $HClO_4$—0.1 M $NaClO_4$, 10^{-5} M Cu(II)	D.p.p. DME	$1 \cdot 10^{-7}$ M (8 p.p.b.)
	A.c. HMDE[a]	$1 \cdot 10^{-8}$ M (0.8 p.p.b.)
	D.p.p. HMDE[a]	$1 \cdot 10^{-8}$ M (0.8 p.p.b.)
1 M $HClO_4$, 10^{-5} M Cu(II)	D.p.p. DME	$1 \cdot 10^{-7}$ M (8 p.p.b.)
0.1 M $HClO_4$—0.1 M $NaClO_4$, 10^{-4} M Cd(II)	A.c. DME	$4 \cdot 10^{-7}$ M (32 p.p.b.)
0.1 M $HClO_4$—0.1 M $NaClO_4$, 10^{-5} M Pb(II), $4.3 \cdot 10^{-2}$ M EDTA	D.p.p. DME	$1 \cdot 10^{-7}$ M (8 p.p.b.)
0.1 M $HClO_4$—0.1 M $NaClO_4$, 10^{-5} M Pb(II), $4.3 \cdot 10^{-2}$ M EDTA	A.c. DME	$2 \cdot 10^{-7}$ M (6 p.p.b.)

Copper(II) and cadmium(II) do not interfere as their reduction potentials are situated near 0.0 V vs. SCE and —0.6 V vs. SCE, respectively, in acidic solutions (Fig. 3). Germanium(IV) can be reduced only in the presence of complex-forming agents such as *o*-diphenols (pyrocatechol, pyrogallol) [23] in acidic medium; in their absence, the trace determination of selenium is not affected.

A potentially serious interference from lead(II) was found. Lead(II) is reduced at about —0.4 V vs. SCE, which is very close to the reduction potential used here for selenium. Thus the selenium peak appears in the descending part of the lead peak and its measurement is impossible at low concentrations. Ethylenediaminetetraacetic acid (EDTA, sodium salt)was found to be suitable for masking lead completely. In this case, 0.1 M $HClO_4$—0.1 M $NaClO_4$ was preferable to a more acidic medium because the solubility of EDTA was slightly higher; any precipitation did not affect the determination. A difference in behaviour during the reduction of selenium should be noted. In a.c. polarography the peak appeared at —0.62 V vs. SCE, i.e. at a more cathodic potential than the previous case. In d.p. polarography, two peaks were obtained at about —0.53 V and —0.62 V vs. SCE, respectively (for ΔE = 20 mV), and the current—concentration relationships were

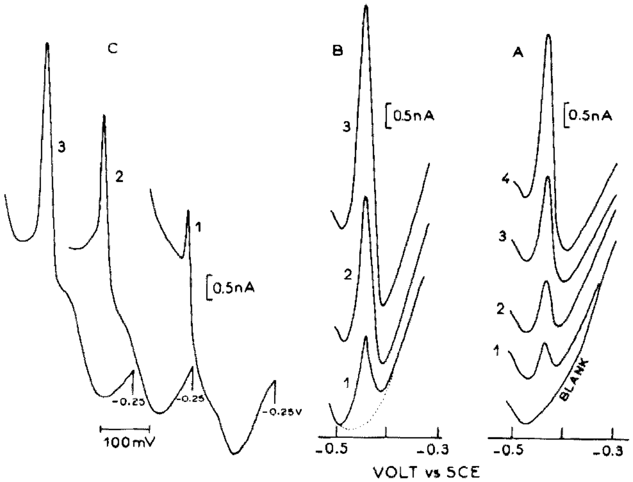


Fig. 3. Polarographic peaks for selenium. (A) In 0.1 M $HClO_4$—0.1 M $NaClO_4$ with a.c.p. and DME in presence of 10^{-4} M Cu(II) and 10^{-5} M Cd(II). Curve (1) 0.3; (2) 0.7; (3) 1.4; (4) $2.4 \cdot 10^{-6}$ M. (B) In 0.1 M $HClO_4$—0.1 M $NaClO_4$ with a.c.p. and DME in presence of 10^{-4} M Cu(II), 10^{-4} M Cd(II) and $4 \cdot 10^{-5}$ M Te(IV). Curve (1) 0.8; (2) 1.9; (3) $3.3 \cdot 10^{-6}$ M. (C) In 0.1 M $HClO_4$—0.1 M $NaClO_4$ with differential pulse and DME in presence of 10^{-4} M Cu(II) and 10^{-5} M Cd(II). Curve (1) 3; (2) 5; (3) $8 \cdot 10^{-7}$ M.

different. The first peak did not obey any simple relation of the type $i = K$ [Se]; the peak height did not increase for $[Se] > 4 \cdot 10^{-7}$ M. The height of the second peak increased linearly with concentration over the range $2 \cdot 10^{-8}$ M—10^{-6} M. (Figs. 4 and 5).

Tables 2 and 3 show the detection limits observed when selenium was measured in the presence of Cu(II), Cd(II), Te(IV), Ge(IV) and Pb(II). Both a.c.p. and d.p.p. are comparable in their performance. Table 4 gives the slopes of the log—log plots of peak height and concentration for the

TABLE 3

Detection limits for selenium in 0.1 M $HClO_4$—0.1 M $NaClO_4$ in presence of Cu(II), Cd(II), Ge(IV) and Te(IV) with the DME

Interfering elements	A.c.p.	D.p.p.
10^{-4} M Cu(II), 10^{-5} M Cd(II)	$4 \cdot 10^{-7}$ M (32 p.p.b.)	$3 \cdot 10^{-7}$ M (24 p.p.b.)
10^{-4} M Cu(II), 10^{-5} M Cd(II), 10^{-4} M Ge(IV)	$3 \cdot 10^{-7}$ M (24 p.p.b.)	$2 \cdot 10^{-7}$ M (16 p.p.b.)
10^{-4} M Cu(II), 10^{-5} M Cd(II), $4 \cdot 10^{-6}$ M Te(IV)	$5 \cdot 10^{-7}$ M (40 p.p.b.)	$2 \cdot 10^{-7}$ M (16 p.p.b.)

TABLE 4

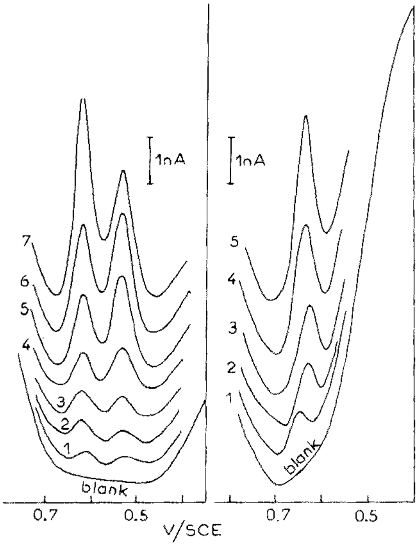
Slopes and linear correlation coefficients of the calibration curves for the determination of selenium in acidic medium[a] (12 points are used for each calculation)

Medium and interfering elements	A.c.p.		D.p.p.	
	DME	HMDE	DME	HMDE
1 M HCl		a = 0.821 r = 1.000	a = 0.884 r = 0.998	a = 0.910 r = 0.998
1 M $HClO_4$		a = 0.965 r = 0.999	a = 1.055 r = 1.000	a = 1.003 r = 1.000
0.1 M $HClO_4$ 0.1 M $NaClO_4$ } Medium A	a = 1.017 r = 0.999	a = 1.275 r = 0.995	a = 1.099 r = 0.999	a = 1.586 r = 0.999
A + 10^{-5} M Te(IV)		a = 0.827 r = 0.984	a = 1.189 r = 1.000	a = 1.159 r = 0.923
A + 10^{-5} M Cu(II)		a = 0.870 r = 1.000	a = 1.134 r = 0.999	a = 1.054 r = 0.995
A + 10^{-4} M Cu(II) + 10^{-5} M Cd(II)	a = 1.011 r = 0.997		a = 0.917 r = 0.998	
A + 10^{-4} M Cu(II) + 10^{-5} M Cd(II) + $4 \cdot 10^{-6}$ M Te(IV)	a = 0.917 r = 0.998		a = 1.029 r = 0.998	
A + 10^{-5} M Pb(II) + $4.3 \cdot 10^{-2}$ M EDTA	a = 1.385 r = 0.998		a = 1.003 r = 0.999	

[a] a = slope; r = correlation coefficient.

different cases studied. These slopes as well as the correlation coefficients calculated by the least squares method show that in certain cases the slope value is not exactly unity. Adsorption of elemental selenium may be responsible for this deviation.

In conclusion, the sensitivity of the selenium determination in acidic medium in the presence of several cations should be emphasized. The use of EDTA is particularly recommended for masking lead(II).



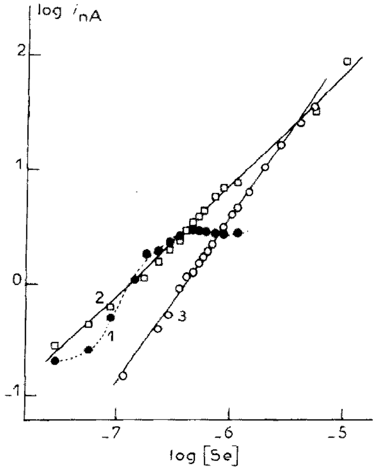


Fig. 4. Polarographic peaks for selenium in presence of lead and EDTA. (A) $[Pb^{2+}] = 10^{-5}$ M; [EDTA] = $4.3 \cdot 10^{-2}$ M; a.c.p. with DME. Concentration of selenium: (1) $2.3 \cdot 10^{-7}$ M; (2) $3.4 \cdot 10^{-7}$ M; (3) $4.6 \cdot 10^{-7}$ M; (4) $6.3 \cdot 10^{-7}$ M; (5) $8.5 \cdot 10^{-7}$ M. (B) $[Pb^{2+}] = 10^{-5}$ M; [EDTA] = $4.3 \cdot 10^{-2}$ M; d.p.p. with DME. Concentration of selenium: (1) $2.86 \cdot 10^{-8}$ M; (2) $5.7 \cdot 10^{-8}$ M; (3) $8.6 \cdot 10^{-8}$ M; (4) $1.14 \cdot 10^{-7}$ M; (5) $2.3 \cdot 10^{-7}$ M; (6) $3.4 \cdot 10^{-7}$ M; (7) $5.7 \cdot 10^{-7}$ M.

Fig. 5. Calibration curves for selenium in presence of EDTA and lead, with d.p.p. and DME. (1) First peak. (2) Second peak. (3) With a.c.p. and DME.

REFERENCES

1 I. I. Nazarenko and A. N. Ermakov, Selenium and Tellurium, Wiley, New York, 1972.
2 K. Schwarz and C. M. Foltz, J. Am. Chem. Soc., 79 (1957) 3292.
3 R. A. Passwater, Fluoresc. News, 7 (1973) 11.
4 G. F. Kirkbright and W. T. S. Sargentili, Atom. Absorpt. Newsl., 8 (1969) 34.
5 K. C. Thompson and D. R. Thomerson, Analyst (London), 99 (1974) 595.
6 J. A. Fiorino, J. W. Jones and S. G. Capar, Anal. Chem., 48 (1976) 120.
7 E. L. Henn, Anal. Chem., 47 (1975) 428.
8 J. Hoste, Anal. Chim. Acta, 2 (1948) 402.
9 J. Hoste and J. Gillis, Anal. Chim. Acta, 12 (1955) 158.
10 K. L. Cheng, Anal. Chem., 28 (1956) 1738.
11 P. A. Parker and L. C. Harvey, Analyst (London), 87 (1962) 558.
12 J. H. Watkinson, Anal. Chem., 38 (1966) 92.
13 H. Mabuchi and H. Nakahara, Bull. Chem. Soc. Jpn, 36 (1963) 151.
14 K. I. Strausz, J. T. Purdham and O. P. Stausz, Anal. Chem., 47 (1975) 2032.
15 F. Wlotzka, Z. Anal. Chem., 215 (1966) 81.
16 D. F. C. Morris and W. Hill, Talanta, 10 (1963) 279.
17 L. Schwaer and K. Suchy, Coll. Czech. Chem. Commun., 7 (1935) 135.
18 J. J. Lingane and L. W. Niedrach, J. Amer. Chem. Soc., 70 (1948) 1997, 4115; 71 (1949) 196.
19 F. Vajda, Acta. Chim. Acad. Sci. Hung., 63 (1970) 257.
20 Alam. A. M. Shafiqul, O. Vittori and M. J. Porthault, Electroanal. Chem., 61 (1975) 191.
21 M. Volaire, O. Vittori and M. J. Porthault, Bull. Soc. Chim. Fr., (1974) 823.
22 M. Volaire, O. Vittori and M. J. Porthault, Anal. Chim. Acta, 71 (1974) 185.
23 V. A. Nazarenko, Germanium, Wiley, New York, 1974.

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THE DETERMINATION OF WAX ESTERS IN LUBE OIL BY INFRARED SPECTROMETRY

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SUMMARY

A simple and rapid method for estimating the content of wax esters in lubricating oils has been developed through the use of isopropanol extraction to concentrate the wax esters. The ratio of the absorption bands at 1740 and 1385 cm^{-1} can be used directly for the determination of wax esters in lube oil samples. The method can be satisfactorily applied at levels down to 1 %, with an overall deviation of less than 10 %; for samples containing as low as 0.5 %, the procedure can be used semi-quantitatively with an error of about 20 %. This infrared method can also be used to determine marine and sulfurized wax esters.

Many instrumental methods for lipid analysis [1] provide only non-specific determinations of constituents such as triglycerides, free fatty acids, phospholipids, and wax esters which may be found in complex mixtures. However, the application of n.m.r. spectrometry to the determination of wax esters in marine oils [2, 3] does not suffer from these difficulties and a very simple rapid operation can give reliable results. Many studies also indicate the potential of i.r. spectrometry in various lipid investigations [4—7]; the i.r. absorption of the carbonyl band has been used for monitoring kinetic changes during the oxidation of various lipids [8, 9]. Three comprehensive reports on the quantitative i.r. spectroscopy of lipids in solution [10—12] have also discussed the theoretical and practical aspects of i.r. spectroscopy as an identification method.

Wax esters have a superior ability to cling to metal surfaces in the form of very thin films [13] and are commonly used in the well-known "Germ" process for improving lubricating oils [14]. However, an effective, rapid procedure for the determination of the relatively low content of wax esters in complex lubricating oils has remained a problem. The analysis of lubricating oil often involves complex mixtures and although i.r. techniques can give information on major components they are not usually sufficiently sensitive for most minor compounds. In this report, a simple rapid i.r. method

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is described for estimating wax esters in lubricating oils at concentrations down to 1 % after the wax esters have been concentrated by a single solvent extraction. Quantitative integrations of the bands corresponding to νCO in dialkyl esters (1740 cm^{-1}) and the CH_3 symmetric scissors (1385 cm^{-1}) are used for calculating the content of wax esters.

EXPERIMENTAL

Materials and apparatus

Commercial samples of spermaceti (BDH, Ltd.) and Duo-Seal pump oil (Welch Scientific Co.) were used as model materials for wax esters (WE) and pure lubricating oil (LO), respectively. The LO was shown to contain only hydrocarbons without any WE additives. Sperm whale (*Physeter catodon*) [2, 15] oil, which contained 78 % WE, and a sulfurized ester oil (Chrysler Canada Ltd., Windsor, Ontario) were also used.

A UNICAM SP-1000 infrared spectrophotometer with a KBr window (5 × 25 cm) taken from a Beckman IR cell was used.

Procedure

A sample of LO (10 g) was weighed out in a 50-ml graduated centrifuge tube (28 × 151 mm) with plastic screw cap. Reagent-grade isopropanol (20 ml) was added to extract the WE from the LO; the tube was shaken gently for about 1 min. Two phases formed within a few minutes after stopping the agitation. After the isopropanol (top) phase had been carefully removed by a Mini-Pet syringe-type pipet, the isopropanol was removed completely with a rotary evaporator. Three drops of the residual WE concentrate were placed on the top part of the KBr window. After the window had been replaced in the cell holder, a thin, uniform oil film was established in the i.r. beam within minutes and the spectra were recorded in triplicate. The ratio between the absorption bands at 1740 and 1385 cm^{-1}, calibrated against WE and LO mixtures could be used directly for determining the content of wax esters in the original lubricating oil. The ratio for the range 0.05—0.4 showed a linear relationship with % WE in lube oil over the range 0.5—4 % (or 5—35 % WE in the extracted oil).

RESULTS AND DISCUSSION

Since the WE content in most lube oils is about 1 % it is necessary to increase the concentration of WE in the sample for i.r. spectrometry. Previous experience with the extraction of WE by ternary solvent systems used for the production of marine wax ester oils [16], led to an investigation of the most suitable solvent for extracting WE from hydrocarbon lubricating oils. The extraction with single solvents such as benzene, chloroform, acetone, hexane, diethyl ether, isopropanol, cyclohexane, toluene, methanol and carbon tetrachloride was evaluated. Isopropanol and acetone showed considerable discrimination in their dissolving power for wax esters and lube oils. The partition coefficients of WE between LO and isopropanol or acetone at room temperature are such that the single-stage recovery of WE is approximately 80 % of that originally present, and the upper solvent phase contains less than 4 % of LO. Because the absorption of the carbonyl group is proposed for the determination of WE by i.r., acetone would have to be removed completely from the extract; high-purity isopropanol is the best solvent for extracting WE from LO in one step. Multiple extractions were also evaluated; the WE content obtained by multiple extractions was only 4 times higher than that in the original sample, and this enrichment did not meet the requirements for a simple determination by i.r.

In the procedure recommended, 20 ml of isopropanol was used to extract the wax esters from a sample (10 g) of LO. By shaking gently for 1 min, separation of the two phases can usually be obtained rapidly without foaming problems. After the isopropanol has been evaporated, about 0.8—0.9 g of WE concentrate, including some LO can be removed from a sample of LO (10 g) which originally contained 1 % WE. The recovery of WE decreases from 84 to 69 % when the WE content is increased from 0.5 to 4 %. Correspondingly, the percentage of WE in the isopropanol concentrate is increased from 6 to 39 %. The overall deviation in this extraction step is less than 5 % for a sample of LO containing 1 % WE. The amounts of WE thus concentrated can be satisfactorily analyzed by i.r. spectrometry (Table 1). The use of 10 ml of isopropanol for the extraction of the WE from a LO sample (10 g) was also investigated. As expected, the concentration of WE in the extract was higher than that obtained with 20 ml of isopropanol, but the percentage recovery and the overall operating errors were much worse.

The i.r. spectra for a pure lube oil, wax esters and mixed reference LO samples which contain 10 or 30 % added WE, are compared in Fig. 1. There is no absorption from 1600—1800 cm^{-1} for a pure lube oil (Fig. 1, left). The band B at 1385 cm^{-1} is the symmetric scissors of $-CH_3$ (δ_s) and $-C(CH_3)_2$ (δ_s) groups [17]. The combination absorption bands from the asymmetric scissors of CH_2 and CH_3 and the symmetric scissors of $-CH_2-O-$ (ester) [17, 18] near 1470 cm^{-1} are not specific enough to be used for WE analysis. The carbonyl absorption band A (νCO) is clearly recorded in Fig. 1 (center) for model WE at 1740 cm^{-1}. For sulfurized WE, band A shifts about 10 cm^{-1} to a lower frequency; this may result from the overlap between carbonyl electrons and the 3*d* orbitals of sulfur [19]. The carbonyl frequencies and intensities of a large number of esters of all kinds have been given by Flett [20]; the carbonyl intensities of esters are remarkably constant, change little with conjugation, and can be used for the determination of WE in lube oils as shown in Fig. 1 (right).

The integrated absorbance of band A is substantial; the ratio of the band heights A/B is even more specific and reproducible, and shows a linear calibration for the WE content whether expressed in terms of isopropanol

TABLE 1

Reproducibility of the determination of wax esters in lube oils by i.r. spectrometry[a]

Sample	No. of analyses	WE content, Wt %	
		Added	Found ± *s*
LO + WE	6	0.5	0.43 ± 0.09
LO + WE	8	1.0	1.11 ± 0.09
LO + Sperm whale oil	8	1.0	0.94 ± 0.08
LO + Sulfurized esters	6	1.0	1.04 ± 0.10
LO + Sperm whale oil	6	2.0	2.13 ± 0.14
LO + WE	6	2.0	1.88 ± 0.08
LO + Sperm whale oil	8	4.0	3.91 ± 0.21
Sample A[b]	6	—	0.81 ± 0.06
Sample B[b]	6	—	1.20 ± 0.11

[a]WE, wax esters; LO, pure lube oil; *s*, standard deviation. [b]Commercial lubricating oils.

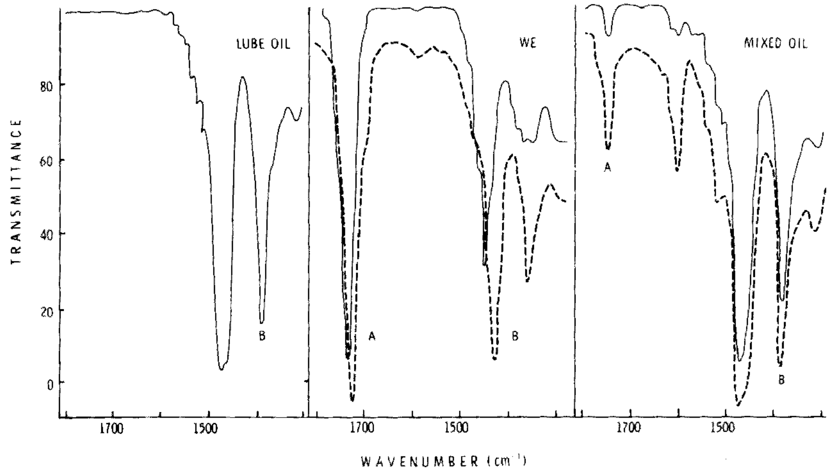

Fig. 1. I.r. spectra for lube oil (left); wax esters (center,—— for Model WE and ----- for sulfurized esters oil); and mixed oil (right, —— sample containing 10 % WE and ---- sample containing 30 % WE). Bands A (1740 cm^{-1}) and B (1385 cm^{-1}) were used.

extracts (6—34 % WE) or in terms of the original LO samples (0.5—4 % WE), respectively; After measurement of the i.r. bands A and B, the original WE content of the lubricating oil can be determined directly from the calibration curve.

The reproducibility and standard error for various LO samples are presented in Table 1. This method can be satisfactorily applied for estimating WE in LO at a level of 1 %, with an overall deviation of less than 10 %; for a sample containing 0.5 % WE the method can be used semi-quantitatively with an error of about 20 %. As shown in Table 1, the procedure can also be used for determining natural marine wax esters and sulfurized wax esters, etc., in LO samples. Extraction with isopropanol followed by i.r. spectrometry is superior to other chemical or chromatographic methods for determination of wax esters in various lubricating oils.

REFERENCES

1 J. C. Dittmer and M. A. Wells, in J. M. Lowenstein (Ed.), Methods in Enzymology, Lipids, Academic Press, New York, 1969, p. 482.
2 P. J. Ke, R. G. Ackman and D. L. Hooper, Anal. Chim. Acta, 69 (1974) 253.
3 P. J. Ke, R. G. Ackman and D. L. Hooper, Anal. Chim. Acta, 78 (1975) 470.
4 N. K. Freeman, J. Am. Oil Chem. Soc., 45 (1968) 798.
5 W. G. de Ruig and G. Dijkstra, Fette, Seifen., Anstrichm., 77 (1975) 211.
6 S. Parkash and J. M. V. Blanchard, Spectrochim. Acta, Part A, 31 (A) (1975) 951.
7 A. M. Baialardo and J. Bellanato, Grasas Aceites (Seville), 26 (1975) 208.
8 K. Bencze, Fresenius Z. Anal. Chem., 274 (1975) 19.
9 W. Zenker, Fette, Seifen. Anstrichm., 77 (1975) 221.
10 P. Schmid, Physiol. Chem. Phys., 7 (1975) 335.
11 P. Schmid and R. N. Steiner, Physiol. Chem. Phys., 7 (1975) 349.
12 P. Schmid and M. Stout, Physiol. Chem. Phys., 7 (1975) 357.
13 D. Swern, Bailey's Industrial Oil and Fat Products, 3rd edn., Interscience, New York, 1964, p. 578.
14 J. E. Southcombe and H. M. Wells, U.S. Pat. 1, 319, 129 (1919).
15 R. G. Ackman, S. N. Hooper, S. Epstein and M. Kelleher, J. Am. Oil Chem. Soc., 49 (1972) 378.
16 P. J. Ke, R. G. Ackman and C. A. Eaton, Can. Inst. Food Sci. Technol. J., 7 (1974) 110.
17 H. A. Szymanski, Interpreted Infrared Spectra. Vol. 1, 2nd edn., Plenum Press, New York, 1968, p. 10.
18 L. J. Bellamy, Advances in Infrared Group Frequencies, Methuen, United Kingdom, 1968, p. 123.
19 A. W. Baker and G. H. Harris, J. Am. Chem. Soc., 18 (1960) 1923.
20 M. St. C. Flett, Spectrochim. Acta, 18 (1962) 1537.

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INSTRUMENTAL ACTIVATION ANALYSIS OF COAL AND FLY ASH WITH THERMAL AND EPITHERMAL NEUTRONS AND SHORT-LIVED NUCLIDES

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SUMMARY

Instrumental neutron activation analysis is applied to the determination of about 25 elements in coals and fly ash by means of nuclides with half-lives of less than 48 h; thermal and epithermal irradiations are used. The results indicate that epithermal activation is preferable for twelve of the elements (Ga, As, Br, Sr, In, Cs, Ba, La, Sm, Ho, W and U). Data for SRM 1632 (coal) and SRM 1633 (fly ash) compare favorably with the results obtained by other investigators.

The combustion of coal is a major source of air pollution, and in the ever-increasing concern regarding environmental contamination, the need has been recognized for versatile and reliable methods for the determination of trace elements in coals and their combustion products. Instrumental neutron activation analysis with thermal neutrons (i.n.a.a.) is one of the most versatile analytical techniques for trace analysis. A comprehensive report by Block and Dams [1] discussed the possibilities offered by this technique for the analysis of coals, based on thermal neutron irradiation and a coaxial Ge(Li) detector. Other investigators [2—6] have reported analyses of coal and fly ash by similar procedures.

In many cases, the number of elements that can be determined with acceptable precision and accuracy may be considerably increased by introducing activation with epithermal neutrons in the reactor by using a cadmium cover to eliminate the thermal neutrons. This technique has found several applications to geological materials [7] and was recently applied to air particulate analysis [8]. No applications of epithermal activation analysis (e.n.a.a.) to coals and ashes have been reported to date. In connection with a large scale investigation of trace elements in coals being conducted by the U.S. Geological Survey, a study was initiated to determine whether e.n.a.a. could provide more information than that obtainable by conventional i.n.a.a. based on thermal neutron activation, and to make comparisons when both techniques were applicable.

Neutron activation analysis often has been criticized in comparison with other techniques, as requiring a long time from the preparation of the samples for irradiation to the completion of the final analysis. In the present paper, emphasis has been placed on methods involving a short irradiation followed by measurements either after a few minutes or on the subsequent day. Nuclides with half-lives of up to two days have been considered.

Thermal neutron activation

Block and Dams [1], in their study of trace elements in coals, listed 13 elements whose contents can be determined by means of nuclides with half-lives shorter than 5 h. From their information on detection limits and concentration ranges in coals, these elements may be classified as follows:

1. elements that can be readily determined in coals by i.n.a.a.: Al, Mg, Cl, Ca, V, Mn, Br;
2. elements that can be determined in a more limited number of coals by i.n.a.a. with satisfactory results: S, Ti, I, Dy;
3. elements which can only occasionally be detected: Cu (by ^{66}Cu), In.

According to our experience, Ba, Sr, and U may be added to group 2, but in these cases, more attractive, longer-lived alternative isotopes exist. If the definition of short-lived activities is extended to 48 h, and a measurement on the day after irradiation is performed, Na, K, and La can be included in group 1, while Cu, Eu and Sm may be added to group 2. This probably represents almost the maximum number of elements that can be determined in coals via short-lived nuclides by i.n.a.a. with the present state of the art. This observation seems to be verified by the number of elements for which results obtained in this manner have been reported for the National Bureau of Standards Coal (SRM 1632).

The situation for fly ash (SRM 1633) is rather similar, except that the halogen concentrations are close to or below the limit of detection. The absence of ^{82}Br contributes to slightly improved conditions for elements measured on the second day, as compared with coals.

Epithermal activation analysis

Activation with epithermal neutrons may often be advantageous if the nuclide of interest has a high I/σ_0 ratio (resonance activation integral to thermal neutron cross-section) in comparison with nuclides giving rise to major activities in the sample on thermal neutron activation. As in many other geological matrices, the major short-lived activities induced in coal and fly ash by thermal neutron activation will, in most cases, be ^{28}Al, ^{56}Mn, and ^{24}Na. Since the stable nuclides from which these radioisotopes are formed show low I/σ_0 ratios compared with a number of nuclides of interest in trace element analysis, the activation of coal and fly ash samples within a cadmium cover could, in many cases, lead to substantial analytical improvement.

The benefit to be achieved by epithermal activation in a certain reactor irradiation position can be described most accurately by means of so-called "advantage factors" [9], which can be calculated from the relevant activation cross-sections and the cadmium ratio of ^{197}Au. In cases where a number of radionuclides may be considered as interfering components, the situation may be adequately described by means of I/σ_0 ratios. Relevant nuclear data for a number of nuclides, formed by (n, γ) reactions, and having half-lives of less than 48 h are presented in Table 1. It appears, from the Table, that e.n.a.a. offers a considerable advantage for the determination of about 25 elements via short-lived nuclides.

The feasibility of the epi-cadmium irradiation technique is not only dependent on nuclear data. It also depends on more practical factors such as the reactor operation schedule, the neutron flux characteristics in the irradiation positions accessible for epi-cadmium work, and the extent of the heat build-up by neutron absorption in the cadmium during the irradiation. The possibility of performing e.n.a.a., especially with short-lived activities which require the use of a pneumatic tube system, may therefore be associated with severe limitations in many reactors.

In the reactor used in the present work, "rabbits" containing cadmium boxes could be inserted during reactor operation, but the return could only take place after reactor shut-down. Including the time necessary for post-irradiation sample preparation, about 35 min elapsed before the activity measurements could be started. The use of nuclides with half-lives shorter than about 20 min was therefore ruled out.

Preliminary tests on samples of coal and fly ash indicated that the epithermal irradiation technique might be advantageous with respect to the following nuclides, with half-lives less than 48 h: ^{72}Ga, ^{76}As, ^{82}Br, ^{85m}Sr, ^{87m}Sr, ^{116m}In, ^{128}I, ^{134m}Cs, ^{139}Ba, ^{140}La, ^{153}Sm, ^{166}Ho, ^{187}W, and ^{239}U. Peaks of ^{233}Th, ^{60m}Co, ^{80}Br and ^{101}Mo—^{101}Tc were also observed but were not suitable for the determination because of poor peak-to-background ratio. A search for peaks of ^{75}Ge, ^{90m}Y, ^{97}Zr, ^{125}Sn, ^{171}Er and ^{176m}Lu was negative. Conditions for the measurement of ^{24}Na, ^{38}Cl, ^{42}K, ^{56}Mn, ^{64}Cu, ^{152m}Eu and ^{165}Dy were estimated to be more favourable after thermal neutron activation.

EXPERIMENTAL

Epithermal activation

Samples of about 100 mg were wrapped in 30-mm × 30-mm sheets of aluminum foil for irradiation. Standards were prepared by evaporating 100-μl aliquots of appropriate solutions on to the aluminum foil, drying at room temperature, and folding. Six samples and one set of standards were wrapped in another aluminum foil and placed inside a 1-mm thick cadmium box (14 mm internal diameter, 10 mm internal height). The cadmium container was wrapped in aluminum foil and irradiated for 30 min in a polyethylene "rabbit" in the pneumatic tube system of the JEEP II reactor

TABLE 1

Nuclear data of interest in the epithermal activation analysis of coals based on short-lived nuclides ($t_{\frac{1}{2}} < 48$ h)

	Nuclide	$t_{\frac{1}{2}}$	σ_0 [10]	I [11]	I/σ_0
Na	^{24}Na	15.0 h	0.528	0.31	0.59
Mg	^{27}Mg	9.5 min	0.038	0.030	0.79
Al	^{28}Al	2.3 min	0.232	0.17	0.73
Cl	^{38}Cl	37.2 min	0.43	0.17	0.40
K	^{42}K	12.4 h	1.48	1.28	0.86
Ca	^{49}Ca	8.8 min	1.1	0.90	0.82
Ti	^{51}Ti	5.8 min	0.179	5.5	37
V	^{52}V	3.76 min	4.90	2.7	0.55
Mn	^{56}Mn	2.58 h	13.3	14	1.1
Ni	^{65}Ni	2.56 h	1.50	0.9	0.6
Cu	^{64}Cu	12.8 h	4.4	5.0	1.1
	^{66}Cu	5.1 min	2.20	2.5	1.1
Zn	^{69m}Zn	13.8 h	0.07	0.24	3.4
Ga	^{72}Ga	14.2 h	4.7	25	5.3
Ge	^{75}Ge	82 min	0.52	0.9	1.7
As	^{76}As	26.5 h	4.4	63	14
Br	^{80}Br	17.6 min	8.4	125	15
	^{82}Br	35.3 h	3.0	50	17
Rb	^{88}Rb	17.8 min	0.12	2.3	19
Sr	^{87m}Sr	2.83 h	0.8	4	5.0
Y	^{90m}Y	3.1 h	0.001	0.9	900
Zr	^{97}Zr—^{97}Nb	17.0 h—74 min	0.05	5.0	100
Nb	^{94m}Nb	6.3 min	0.15	8.0	53
Mo	^{101}Mo—^{101}Tc	14.6 min—14 min	0.20	3.9	20
In	^{116m}In	54.0 min	161	2600	16
Sn	^{125m}Sn	9.7 min	0.14	9	64
I	^{128}I	25.0 min	6.2	150	24
Cs	^{134m}Cs	2.9 h	2.6	30	12
Ba	^{135m}Ba	29 h	0.16	24	15
	^{139}Ba	82.9 min	0.35	0.3	0.9
La	^{140}La	40.2 h	9.0	11	1.2
Nd	^{149}Nd	1.8 h	2.5	17	6.8
Sm	^{153}Sm	47.0 h	210	2900	14
	^{155}Sm	23 min	5.5	27	4.9
Eu	^{152m}Eu	9.2 h	2800	2600	0.93
Gd	^{159}Gd	18 h	3.5	80	23
Dy	^{165}Dy	139 min	2600	800	0.31
Ho	^{166}Ho	26.9 h	61.5	660	11
Er	^{171}Er	7.5 h	6	35	5.8
Yb	^{177}Yb	1.9 h	5.5	7	1.3
Lu	^{176m}Lu	3.69 h	18	600	33
W	^{187}W	23.9 h	37	420	11
Th	^{233}Th	22.2 min	7.4	82	11
U	^{239}U	23.5 min	2.72	280	103

(Kjeller, Norway) at a thermal flux of about $1.5 \cdot 10^{13}$ n cm^{-2} s^{-1} and a cadmium ratio of ^{197}Au of 2.9. Insertion took place 30 min before reactor shut-down and the "rabbit" was retained in the reactor for another 20 min before return to the laboratory. After unpacking, the samples were weighed and wrapped in inactive aluminum foil. Activities were measured with a system consisting of two coaxial Ge(Li) detectors (5 % relative efficiency, 2.5 keV FWHM and 3 % relative efficiency, 3.0 keV FWHM, respectively) with associated electronics, interfaced to a NORD I computer (16 K, 16 bit). Two samples or standards were counted simultaneously for 10 min. The distance between samples and detector was so adjusted that the dead-time did not exceed 15 %. Dead-time corrections were made by means of precision pulse generators, and the peak areas were calculated by the method of Covell [12]. In some cases only one channel on each side of the top channel was included in the peak area in order to avoid interferences from adjacent peaks. The samples were re-counted after an interval of about 24 h. The radionuclides, decay times, and γ-energies involved are given in Table 2.

Activation without cadmium cover

Samples of about 100 mg were sealed in small envelopes of polyethylene foil. Standards were made by absorbing 50 μl of a solution on to filter paper and sealing in the same sort of polyethylene envelopes. Two samples or standards were irradiated in each "rabbit". The irradiation time was 5 min

TABLE 2

Elemental concentration in NBS Coal (SRM 1632) and NBS Fly ash (SRM 1633) by instrumental activation analysis with epithermal neutrons (p.p.m.)

Element	Nuclide measured	γ-Energy (keV)	Decay time(h)	NBS 1632		NBS 1633	
				Mean[a]	s_r (%)	Mean[a]	s_r (%)
Ga	^{72}Ga	630	∿ 24	6.1	10.7	40.3	5.0
		834	24	5.8	7.7	40.7	3.0
As	^{76}As	559	24	6.5	18.5	58.0	3.5
Br	^{82}Br	618	24	19.5	1.5	7.7	19.5
Sr	^{85m}Sr	231	∿ 1	165	12.7	1360	8.1
	^{87m}Sr	388	1	161	5.6	1430	4.2
In	^{116m}In	417	1	0.0169	7.1	0.128	6.3
		1099	1	0.0178	7.8	0.118	3.4
Cs	^{134m}Cs	127	1	1.36	7.4	8.2	11.0
Ba	^{139}Ba	165	1	338	4.1	2540	2.0
La	^{140}La	1596	∿ 24	11.4	4.3	81.2	4.0
Sm	^{153}Sm	69	24	1.38	7.2	11.4	14.0
Ho	^{166}Ho	80	24	0.24	12.5	1.94	6.7
W	^{187}W	685	24	0.79	21.5	4.2	9.5
U	^{239}U	74	∿ 1	1.46	1.4	12.7	4.0

[a] Mean of 5 separate determinations.

for coal samples and 1 min for ash samples. After 20 min, measured with a stopwatch, the samples were counted for 10 min as described above. The interval between subsequent irradiations was 15 min to allow sufficient time for concentration print-outs and changing of samples. After 24 h, the samples were re-counted, in the same sequence, to avoid time-consuming calculations of decay corrections. The radionuclides, decay times and γ-energies used for this part of the investigation are listed in Table 3.

RESULTS AND DISCUSSION

In order to compare the two methods and obtain a measure of the precision and to some extent the accuracy to be expected on application to coals and ashes, the standard reference materials coal (SRM 1632) and fly ash (SRM 1633) from the U.S. National Bureau of Standards were investigated. Five replicates of each sample were analyzed and the results are given in Tables 2 and 3 for the epithermal and thermal neutron irradiations, respectively. In Tables 4 and 5, the "best" values from the present work, as indicated in the following discussion, are compared with literature values for SRM 1632 and SRM 1633. The methods also have been

TABLE 3

Elemental concentrations in NBS Coal (SRM 1632) and NBS Fly ash (SRM 1633) by instrumental activation analysis with thermal neutrons

Element	Nuclide measured	γ-Energy (keV)	Decay time	NBS 1632		NBS 1633	
				Mean[a]	s_r (%)	Mean[a]	s_r (%)
Na, p.p.m.	^{24}Na	2756	1 d	380	6.5	2830	4.8
Mg, %	^{27}Mg	1014	20 min	0.17	17.6	1.78	11.2
Al, %	^{28}Al	1780	20 min	1.74	2.3	12.35	2.0
Cl, p.p.m.	^{38}Cl	2167	20 min	844	4.4	—	
K, %	^{42}K	1524	1 d	0.298	8.0	1.80	7.2
Ca, %	^{49}Ca	3084	20 min	0.350	8.0	4.69	3.0
Ti, %	^{51}Ti	320	20 min	0.089	5.6	0.70	4.3
V, p.p.m.	^{52}V	1434	20 min	35.0	8.3	237	8.4
Mn, p.p.m.	^{56}Mn	1811	20 min	41.1	8.8	488	2.9
Cu, p.p.m.	^{64}Cu	511[b]	1 d	15.0	8.0	115	7.0
Br, p.p.m.	^{80}Br	617	20 min	14	14.3	—	
Sr, p.p.m.	^{87m}Sr	388	20 min	131	17.6	1200	25
I, p.p.m.	^{128}I	443	20 min	2.9	10.3	—	
Ba, p.p.m.	^{139}Ba	165	20 min	274	11.3	2580	6.6
La, p.p.m.	^{140}La	1596	1 d	10.3	10.7	91	7.7
Eu, p.p.m.	^{152m}Eu	122	1 d	0.299	11.0	2.44	7.8
Dy, p.p.m.	^{165}Dy	94	20 min	1.12	5.4	9.4	5.3
U, p.p.m.	^{239}U	74	20 min	1.52	7.2	13.5	8.9

[a] Mean of five separate determinations.

[b] After subtraction of contribution from pair production associated with ^{24}Na.

TABLE 4

Elemental concentrations in NBS Coal (SRM 1632). Comparison of present data with literature values

Element	Present work preferred values[a]	Ondov et al. [3]	Nadkarni [5]	Ruch et al. [14]	Klein et al. [6]	Chattopadhyay and Jervis [13]	Millard and Swanson [4]	NBS Certified value
Na, p.p.m.	380 ± 25 *T*	414 ± 20	347 ± 32	383 ± 14	390	351 ± 30	410	
Mg, %	0.17 ± 0.03 *T*	0.20 ± 0.05	0.15 ± 0.03		0.248	0.160 ± 0.015		
Al, %	1.74 ± 0.04 *T*	1.85 ± 0.13	1.76 ± 0.31		1.90			
Cl, p.p.m.	844 ± 37 *T*	890 ± 125	945 ± 35	846 ± 44	1000	930 ± 48		
K, %	0.298 ± 0.024 *T*	0.28 ± 0.03	0.278 ± 0.023	0.29 ± 0.02	0.290		0.29	
Ca, %	0.350 ± 0.028 *T*	0.43 ± 0.05	0.43 ± 0.02		0.44			
Ti, %	0.089 ± 0.005 *T*	0.104 ± 0.011	0.084 ± 0.017		0.093	0.0973 ± 0.0050		0.080[b]
V, p.p.m.	35.0 ± 2.9 *T*	36 ± 3	32.7 ± 3.4		40 ± 3	33.9 ± 3.0		35 ± 3
Mn, p.p.m.	41.1 ± 3.6 *T*	43 ± 4	40.3 ± 6.9	43.7 ± 1.8	46 ± 3	47.1 ± 4.1	46	40 ± 3
Cu, p.p.m.	15.0 ± 1.2 *T*				18			18 ± 2
Ga, p.p.m.	5.8 ± 0.4 *E*			5.15 ± 0.3	8.5			
As, p.p.m.	6.5 ± 1.2 *E*	6.5 ± 1.4	4.61 ± 0.32	8.9 ± 0.5	5.5	5.25 ± 0.37		5.9 ± 0.6
Br, p.p.m.	19.5 ± 0.3 *E*	19.3 ± 1.9	15.2 ± 1.4	18.2 ± 2.3	14.2			
Sr, p.p.m.	161 ± 9 *E*	161 ± 16	1.02 ± 0.05	145 ± 9	144	1.33 ± 0.1	129	
In, p.p.m.	0.0169 ± 0.0012 *E*	0.20 ± 0.12		0.22 ± 0.02	0.07	0.23 ± 0.02		
I, p.p.m.	2.9 ± 0.3 *T*		6.63 ± 1.2	2.8 ± 0.4				
Cs, p.p.m.	1.36 ± 0.10 *E*	1.4 ± 0.1	1.32 ± 0.11	1.8 ± 0.3	1.4	0.35 ± 0.04	2.6	
Ba, p.p.m.	338 ± 14 *E*	352 ± 30	311 ± 25	366 ± 34	405	314 ± 20	280	
La, p.p.m.	11.4 ± 0.5 *E*	10.7 ± 1.2	7.89 ± 0.15	11.3 ± 0.4	10.5		11.3	
Sm, p.p.m.	1.38 ± 0.10 *E*	1.7 ± 0.2	1.66 ± 0.16	1.8 ± 0.1			1.6	
Eu, p.p.m.	0.299 ± 0.022 *T*	0.33 ± 0.04	0.37 ± 0.02	0.41 ± 0.03	0.21		0.4	
Dy, p.p.m.	1.12 ± 0.06 *T*		1.38 ± 0.09	1.3 ± 0.5			1.4	
Ho, p.p.m.	0.24 ± 0.03 *E*							
W, p.p.m.	0.79 ± 0.17 *E*	0.75 ± 0.17		0.74 ± 0.3				
U, p.p.m.	1.46 ± 0.02 *E*	1.41 ± 0.07	1.2 ± 0.1	1.46 ± 0.35	1.26	1.37 ± 0.08	1.43	1.4 ± 0.1

[a] *T* = thermal neutron activation, *E* = epithermal neutron activation. [b] Information value.

TABLE 5

Elemental concentrations in NBS Fly ash (SRM 1633). Comparison of present data with literature values

Element	Present work, preferred value[a]	Ondov et al. [3]	Nadkarni [5]	Klein et al. [6]	Chattopadhyay and Jervis [13]	Millard and Swanson [4]	NBS Certified value
Na, p.p.m.	2830 ± 140 *T*	3200 ± 400	3300 ± 200		3400 ± 300	3400	3070
Mg, %	1.78 ± 0.20 *T*	1.8 ± 0.4	1.52 ± 0.06		1.48 ± 0.1		1.98
Al, %	12.35 ± 0.25 *T*	12.7 ± 0.5	14.3 ± 1.1	12.5			
K, %	1.80 ± 0.13 *T*	1.61 ± 0.15	1.78 ± 0.23	1.8		1.77	1.72
Ca, %	4.69 ± 0.14 *T*	4.7 ± 0.6	4.21 ± 0.09	4.34	3.92 ± 0.28		
Ti, %	0.70 ± 0.03 *T*	0.74 ± 0.03	0.61 ± 0.02	0.642	0.723 ± 0.04		
V, p.p.m.	237 ± 20 *T*	235 ± 15	223 ± 9.9	240	208 ± 12		214 ± 8
Mn, p.p.m.	488 ± 14 *T*	496 ± 19	464 ± 1.4	460	495 ± 25	540	493 ± 7
Cu, p.p.m.	115 ± 8 *T*			133			
Ga, p.p.m.	40.3 ± 2.0 *E*			49			
As, p.p.m.	58.0 ± 2.0 *E*	58 ± 4	67.6 ± 0.9	54	60.7 ± 2.6		61 ± 6
Br, p.p.m.	7.7 ± 1.5 *E*	12 ± 4	7.52 ± 0.46	6.0			
Sr, p.p.m.	1430 ± 60 *E*	1700 ± 300	1406 ± 80	1301	1373 ± 95	1390	1380
In, p.p.m.	0.128 ± 0.008 *E*	0.32 ± 0.10			0.28 ± 0.03		
Cs, p.p.m.	8.2 ± 0.9 *E*	8.6 ± 1.1	5.81 ± 1.4		0.63 ± 0.06	9.4	
Ba, p.p.m.	2540 ± 50 *E*	2700 ± 200	2700 ± 200	2780	2610 ± 210	2490	
La, p.p.m.	81.2 ± 3.3 *E*	82 ± 2	64.1 ± 1.6	82		80	
Sm, p.p.m.	11.4 ± 1.6 *E*	12.4 ± 0.9	13.6 ± 0.88	15			
Eu, p.p.m.	2.44 ± 0.19 *T*	2.5 ± 0.4	2.62 ± 0.05	2.86		3.1	
Dy, p.p.m.	9.4 ± 0.5 *T*		10.9 ± 0.0			10.2	
Ho, p.p.m.	1.94 ± 0.13 *E*						
W, p.p.m.	4.2 ± 0.4 *E*	4.6 ± 1.6					
U, p.p.m.	12.7 ± 0.5 *E*	12.0 ± 0.5	11.3 ± 0.3	11.8		11.7	11.6 ± 0.2

[a] *T* = thermal neutron activation, *E* = epithermal neutron activation.

applied to a study of the fractionation of trace elements during combustion in coal-fired power plants, the results of which will be reported elsewhere [15].

A separate discussion of each of the elements studied is given in the following paragraphs.

Na, Mg, Al, Cl, K, Ca, Ti, V, Mn

These elements were determined by thermal neutron irradiation, and the results agree with previously published values. The precision observed in this work is similar to that reported by other investigators. I.n.a.a. seems to yield rapid, reliable results for Na, Al, V, and Mn in coal and fly ash, and for Cl in coal. For K, Ca, and Ti, the situation appears to be less satisfactory and for Mg, relatively poor results can be expected. Chlorine was not detected in the fly ash samples. The only point where the present procedure deviates from most previous work with regard to the above elements is that Al is determined along with 12 other elements in a 10 min count starting 20 min after the irradiation so as to avoid making two different counts for this group of elements. The activity of ^{28}Al in the first few minutes of the counting period is still sufficiently high to allow a precise determination (cf. Tables 2 and 3), but it is not so high as to cause a major contribution to the dead-time. The only element in this group that might be more advantageously determined by e.n.a.a. is titanium. Because of the short half-life of ^{51}Ti (5.8 min), e.n.a.a. was not attempted for this element.

Cu, Ga, As, Br, Sr, In, I, Cs, Ba

Copper. Copper as determined by i.n.a.a. has not been reported previously for these materials. The result obtained in this work for SRM 1632, after proper correction for the interferences from ^{24}Na to the 511-keV peak of ^{64}Cu, is in agreement with the certified value within error limits.

Gallium. The determination of gallium in SRM 1632 and SRM 1633 by i.n.a.a. has not been previously reported. The determination of gallium can readily be accomplished by e.n.a.a. because of the favorable I/σ_0 of ^{71}Ga relative to that of ^{23}Na. Our value of 5.8 ± 0.4 p.p.m. for SRM 1632 is in fair agreement with the 5.15 ± 0.3 p.p.m. value by Ruch et al. [14] obtained by a radiochemical neutron activation procedure.

Arsenic. The e.n.a.a. determination of arsenic in both the coal and fly ash sample was accomplished after only a 24-h decay. In order to obtain similar results by thermal neutron activation, it would have been necessary to wait for an additional 2—3 days before making the measurements.

Bromine. Bromine was determined easily in both samples via ^{82}Br after only 24 h decay by means of e.n.a.a. At this time, the determination by thermal neutron activation was more difficult, especially in the case of the fly ash sample. An attempt to determine bromine by means of ^{80}Br after thermal neutron activation was not successful.

Strontium. Two different isotopes (^{85m}Sr and ^{87m}Sr) could be used for the determination by e.n.a.a. The results obtained by means of ^{87m}Sr appeared to show higher precision for both the materials. The values for SRM 1633 are in good agreement with the certified value. By thermal neutron activation, very poor results were obtained with ^{87m}Sr, and ^{85m}Sr could not be detected.

Indium. Indium is especially suitable for analysis by e.n.a.a. The advantage to be obtained relative to ^{56}Mn, the major interfering nuclide, is about a factor of 15. This makes it possible to determine indium in coals with a precision of about 10 % and in ashes with a precision of about 5 %, without the necessity for a chemical separation. Both the 417- and 1099-keV peaks are applicable. Attempts to use the 1293-keV peak gave systematically high results which may be associated with the presence of trapped ^{41}Ar which has a coinciding γ-ray.

According to Block and Dams [1], the concentration level of indium in coals is of the order of 0.01—0.03 p.p.m. Application of e.n.a.a. to U.S. coals gave values of similar order here. Several investigators have reported values around 0.2 p.p.m. for the indium content of SRM 1632. We believe that those results may be erroneous, and may be due to spectral interferences, contamination, or other sources of systematic errors.

Iodine. The iodine content of SRM 1632, determined by thermal neutron activation, was in agreement with the value reported by Ruch et al. [14]. Theoretically, the sensitivity for iodine determination in coals and ashes should be about a factor of 20 improved by using e.n.a.a. In attempts to prove this, difficulties were encountered from volatilization of ^{128}I from the standards during irradiation. This experiment was therefore discontinued.

Cesium. The determination of cesium by neutron activation analysis is usually based on 2.3-y ^{134}Cs, which shows a high sensitivity by i.n.a.a. and even better for e.n.a.a. In the present work, the cesium determination by e.n.a.a. was shown to be feasible by means of the short-lived isotope ^{134m}Cs. The present results compare well with the values from the joint study by Ondov et al. [3].

Barium. Although the determination of barium via ^{139}Ba in these samples by i.n.a.a. is possible, the reproducibility was found to be significantly improved by e.n.a.a., as was expected from the nuclear properties of ^{138}Ba.

La, Sm, Eu, Dy, Ho, W, U

Lanthanum. The results from this study agree with the values in the literature. E.n.a.a. appears to show better precision than i.n.a.a. when the measurements are carried out after one day, primarily because of a higher ^{140}La/^{24}Na ratio.

Samarium. The present values, based on measurement of the 69-keV γ-ray after epithermal irradiations, are slightly lower than most of the literature values. This could be related to spectral interference from ^{239}Np when the 103-keV γ-ray of ^{153}Sm was measured in some of the other work. This interference could be significant because the uranium content of the samples is fairly high.

Europium and dysprosium. These elements are determined best by thermal neutron activation. The present data agree with most of the literature values, except for dysprosium in SRM 1632, where our value is slightly lower.

Holmium. The present data for holmium seem to be the first reported for SRM 1632 and SRM 1633. The main reason for this is primarily the advantage obtained by using e.n.a.a.

Tungsten. Tungsten can be determined in many coals and ashes by i.n.a.a. and several values for SRM 1632 and SRM 1633 have been reported. Also in this case, e.n.a.a. is to be preferred because the I/σ_0 ratio of ^{186}W is almost 20 times that of ^{23}Na.

Uranium. This element is one of the very best cases for e.n.a.a. The "advantage factor" of ^{239}U relative to the major interfering nuclide ^{56}Mn is calculated to be 24 under the present conditions. Even though uranium could be determined in SRM 1632 and SRM 1633 by i.n.a.a. with this nuclide, the results obtained by e.n.a.a. show significantly greater precision.

Shielding effects

The possibility of shielding effects should never be overlooked in activation analysis. Possible errors from such effects in e.n.a.a. have been discussed elsewhere [7] in the case of silicate rocks. Since the elemental composition of coal ash and silicate rocks is somewhat similar, the shielding effects should also be insignificant in this case and even more so in the case of the coals because of the low neutron capture cross-section of carbon. However, carbon is a good neutron moderator and one might expect some moderation of epithermal neutrons in the samples. The possible effects of such neutron moderation seem to be negligible, however, since results from the two different techniques appear to be in good agreement both in the case of a nuclide with a very high I/σ_0 ratio (^{238}U) and a nuclide with a fairly low value for this ratio (^{139}La). In case of larger sample weights, neutron moderation effects may prove to be significant. The thermal neutrons thus produced would be likely to be absorbed by the cadmium, and the net result might be a lower exposure of epithermal neutrons to the samples than to the standards. In any case, errors of this kind could be avoided by using a coal as a standard.

As demonstrated in this work and other recent investigations, many short-lived nuclides may be advantageously used in the multi-element analysis of coal and its combustion products by i.n.a.a. The introduction of e.n.a.a. as a supplementary technique extends the number of elements that can be determined by the purely instrumental approach and facilitates an improvement in the results obtained for a number of the elements compared with those obtained by i.n.a.a. with thermal neutrons.

REFERENCES

1 C. Block and R. Dams, Anal. Chim. Acta, 68 (1973) 11.
2 R. R. Ruch, H. J. Gluskoter and N. F. Shimp, Occurrence and Distribution of Potentially Volatile Trace Elements in Coals, Environmental Geology Notes No. 72, Illinois State Geological Survey, Urbana, 1974.
3 J. M. Ondov, W. H. Zoller, I. Omez, N. K. Aras, G. E. Gordon, L. A. Rancitelli, K. H. Abel, R. H. Filby, K. R. Shah and R. C. Ragaini, Anal. Chem., 47 (1975) 1102.
4 H. T. Millard and V. E. Swanson, Trans. Am. Nucl. Soc., 21 (1975) 108.
5 R. A. Nadkarni, Radiochem. Radioanal. Lett., 21 (1975) 161.
6 D. H. Klein, A. W. Andren, J. A. Carter, J. F. Emery, C. Feldman, W. Fulkerson, W. S. Lyon, J. C. Ogle, Y. Talmi, R. I. van Hook and N. Bolton, Environ. Sci. Technol., 9 (1975) 973.
7 E. Steinnes, in A. O. Brunfelt and E. Steinnes (Eds.), Activation Analysis in Geochemistry and Cosmochemistry, Universitetsforlaget, Oslo 1971, p. 113.
8 M. Janssens, B. Desmat, R. Dams and J. Hoste, J. Radioanal. Chem., 26 (1975) 305.
9 D. Brune and K. Jirlow, Nukleonik, 6 (1964) 272.
10 R. Sher, in Handbook on Nuclear Activation Cross-Sections, pp. 1—13, Tech. Rept. Series No. 156, International Atomic Agency, Vienna, 1974.
11 H. Albinsson, in Handbook on Nuclear Activation Cross-Sections, pp. 15—86, Tech. Rept. Series No. 156, International Atomic Agency, Vienna, 1974.
12 D. F. Covell, Anal. Chem., 31 (1959) 1785.
13 A. Chattopadhyay and R. E. Jervis, Anal. Chem., 46 (1974) 1630.
14 R. R. Ruch, R. A. Cahill, J. K. Frost, L. R. Camp and H. J. Gluskoter, Trans. Am. Nucl. Soc., 21 (1975) 107.
15 J. J. Rowe, E. Steinnes and P. Zubovic, to be published.

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SPECTROPHOTOMETRIC DETERMINATION OF FLOTATION COLLECTORS AND ORGANIC REAGENTS IN ORE TREATMENT PROCESS LIQUORS AND EFFLUENTS WITH AN ATOMIC ABSORPTION SPECTROMETER

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SUMMARY

An atomic absorption spectrometer has been adapted to measure the absorbance of solutions of flotation reagents (e.g. xanthate, mercaptobenzothiazole, dithiophosphate, and Z-200) in the concentration range 0—10 mg l^{-1} in aqueous and non-aqueous solvents in the u.v. and visible regions. The absorbance values obtained are similar to those from a u.v.—visible spectrophotometer and straight-line calibration graphs are obtained. Hollow-cathode lamps emitting the desired wavelengths can be selected from wavelength tables of atomic lines. This technique allows a metallurgical analytical laboratory to extend its range of determinations without additional cost by the use of an a.a.s. unit as a u.v.—visible spectrometer.

Historically, the preferred technique for determinations of collector residuals (e.g. xanthate) in flotation liquors is by direct ultraviolet absorption spectrometry [1,2], which can also be used for mercaptobenzothiazole (MBT) [3]. Extraction with organic solvents and u.v. spectrometry on the extract can be used [4] for *O*-isopropyl-*N*-ethylthiocarbamate and MBT [5]. Dithiophosphates can be determined by extraction of a copper complex and spectrometry in the visible range [6].

These determinations can be made with any u.v.—visible spectrophotometer, though special purpose spectrophotometers have been made for xanthate determinations [7]. Nevertheless, all these instruments are relatively expensive, and their purchase for an occasional determination of collector residual may not be economical in a mining or metallurgical laboratory involved primarily in routine analysis for metals. Such a laboratory could more reasonably be expected to have available one or more atomic absorption (a.a.) spectrometers. The purpose of this paper is to demonstrate the application of an a.a. spectrometer as a u.v.—visible spectrometer to the general determination of flotation collectors and other organic reagents in ore treatment process liquors and plant effluents.

Hildon [8] used a vanadium hollow-cathode lamp in an a.a. spectrometer to determine titanium by measuring the absorbance of the titanium—hydrogen peroxide complex in aqueous solution. B. S. Rawling (personal communication) used a tin lamp/a.a.s. combination for xanthate determinations in aqueous solution; at Kanmantoo Mines Ltd., a copper lamp/a.a.s. combination is used to determine Z-200 in cyclohexane extracts.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Varian-Techtron AA 1000 spectrometer. Comparative absorbance measurements were made with a Unicam SP800A spectrophotometer after its absorbance calibration had been checked with 10.0 g l^{-1} potassium nitrate solution [9]. In all this work a 1-cm quartz cell was used. A cell-holding device was constructed and fitted in place of the a.a. burner block; the device was positioned so that the cell was always located in the same position, and light from the hollow-cathode lamp passed through the centre of the cell.

Reagents

The main reagents used were potassium nitrate (AR), chloroform (AR), cyclohexane (spectro-quality), potassium ethyl xanthate (KEX; freshly purified by dissolution in acetone and precipitation with sodium-dried diethyl ether), purified [3] mercaptobenzothiazole (MBT), Z-200 reagent (Dow Chemical Co., principal component *O*-isopropyl-*N*-ethylthiocarbamate), Sodium Aerofloat (American Cyanamid Co., principal component sodium *O,O*-diethylphosphorodithioate), phenol (AR), and cresylic acid TD (Union Carbide Co.).

Procedure

Both spectrometers were set up in accordance with the manufacturers' instructions. The required hollow-cathode lamp was fitted to the a.a. spectrometer, and operated under the conditions recommended by the manufacturer.

Stock solutions containing 100 mg l^{-1} of each flotation collector were prepared in an appropriate solvent and were diluted to 0—10 mg l^{-1} as desired for measurement. Potassium nitrate solutions were made up to 10.0 g l^{-1} and diluted as required.

The absorption spectrum of each solution in a 1-cm cell was obtained with the Unicam spectrophotometer and the value of the absorbance maximum was read from the graph. An appropriate blank was always used in the reference cell. The a.a. unit was used to measure the absorbance of each solution in a 1-cm cell at specified wavelengths after first zeroing the instrument with the appropriate blank solution. The zero was checked, and adjusted where necessary, between measurements. The values reported are the mean of up to three measurements taken on different days using freshly prepared solutions.

RESULTS AND DISCUSSION

Table 1 lists the absorbance values in a 1-cm cell for various solutions as determined with the AA 1000 spectrometer and with the Unicam spectrophotometer. The selection of particular hollow-cathode lamps for measurement is discussed below. Plots (not shown here) of absorbance vs. concentration for all the groups of data in Table 1 showed that a straight-line relationship was obtained in each case (i.e. up to about 0.9 absorbance).

Potassium nitrate is not a flotation reagent, but it is very useful for absorbance calibrations at about 300 nm [2,7,9]. With potassium nitrate, the absorbance values for given concentrations were the same, within experimental error, for the three hollow-cathode lamps used (tin, nickel, and iron) in spite of differences of nearly 2 nm in the wavelength of measurement. This is because the absorption maximum is fairly broad [2, 9]. The absorbance values obtained for potassium nitrate with the Unicam instrument were slightly, but consistently, less than those obtained with the a.a. unit even though the value for 10,000 mg l^{-1} is within the limits quoted by Edisbury [9] for a properly calibrated spectrometer (i.e. 0.705 ± 0.005 *A* at 302 nm). The higher values obtained for potassium nitrate with the a.a. unit were attributed to two causes. Firstly, the a.a. unit effectively eliminates stray light, which is almost always present in u.v.—visible spectrophotometers. Secondly, the use of a hollow-cathode lamp and a grating monochromator gives radiation with a very narrow band width; this results in higher measured absorbances.

For xanthate, as typified by potassium ethyl xanthate, an iron or nickel lamp gave the same absorbance values as those obtained with the Unicam unit. Since all alkyl xanthates have the same molar absorptivity [2] at 301 nm this result can be applied to any of the xanthates used in mineral processing.

MBT has a pH-dependent u.v. absorption spectrum [3]. Analytical wavelengths for MBT determination are 310 nm (one of the isosbestic points), 310 nm in alkaline solution ($pH > 10$), or 323 nm in acid solution ($pH < 2$) [3]. Results in Table 1 show that MBT can be determined in either alkaline or acid solution with an a.a. spectrometer and an appropriate lamp. Absorbance values were different from those obtained with the Unicam spectrophotometer for reasons given above. The absorbance values obtained with the copper hollow-cathode lamp were slightly lower, as measurements were not made at the absorption maximum. In alkaline solution, an absorption maximum at 233 nm can be used for determining MBT in water, but not in plant solutions because of interference [3]. Details are not shown here, but a straight line calibration was obtained at 233 nm up to 7.5 mg l^{-1} MBT with an aluminium hollow-cathode lamp. MBT can

TABLE 1

Comparison of absorbance values of various solutions in 1-cm cells determined with an a.a. spectrometer and a u.v.—visible spectrophotometer

Reagent	Reagent concn. (mg l^{-1})	Solvent	Absorbance with a.a.s.			Absorbance with u.v. spectrometer
			Lamp 1^a	Lamp 2^a	Lamp 3^a	
			(Fe lamp, 301.9 nm)	(Sn lamp, 300.9 nm)	(Ni lamp, 300.2 nm)	(302 nm^b)
KNO_3	0	H_2O	0.00	0.00	0.00	0.00
	500		n.d.	0.04	n.d.	n.d.
	1000		0.07	0.08	0.07	0.07
	2500		0.18	0.18	0.175	0.17
	5000		0.355	0.36	0.355	0.35
	7500		0.54	0.535	0.535	0.52
	10000		0.71	0.72	0.71	0.70
			(Fe lamp, 301.9 nm)	(Ni lamp, 300.2 nm)		(301 nm^b)
KEX	0	Na_2CO_3	0.00	0.00		0.00
	2.0	100 mg l^{-1}	0.22	0.22		0.21
	4.0		0.435	0.44		0.43
	6.0		0.655	0.66		0.645
	8.0		0.87	0.875		0.87
			(Al lamp, 309.3 nm)	(Zn lamp, 307.6 nm)		(310 nm^b)
MBT	0	NaOH	0.00	0.00		0.00
	1.0	1 g l^{-1}	0.12	0.11		0.11
	2.5		0.285	0.28		0.275
	5.0		0.575	0.56		0.55
	7.5		0.86	0.835		0.84
			(Li lamp, 323.3 nm)	(Cu lamp, 324.8 nm)		(323 nm^b)
MBT	0	HCl	0.00	0.00		0.00
	1.0	10 ml l^{-1}	0.16	0.145		0.145
	2.5		0.395	0.360		0.37
	5.0		0.765	0.725		0.755
			(Cu lamp, 327.4 nm)	(Ag lamp, 328.1 nm)		(329 nm^b)
MBT	0	$CHCl_3$	0.00	0.00		0.00
	1.0		0.175	0.165		0.16
	2.0		0.34	0.33		0.325
	3.0		0.495	0.49		0.47
	4.0		0.67	0.665		0.655

TABLE 1 (continued)

Reagent	Reagent concn. (mg l^{-1})	Solvent	Absorbance with a.a.s.			Absorbance with u.v. spectrometer
			Lamp 1^a	Lamp 2^a	Lamp 3^a	
			(Ca lamp, 422.7 nm)			(418 nm^b)
Na Aerofloat (as copper complex)	0	CCl_4	0.00			0.00
	10		0.04			0.055
	20		0.095			0.09
	30		0.135			0.135
	40		0.185			0.185
			(Cu lamp, 244.2 nm)	(Au lamp, 242.8 nm)		(242 nm^b)
Z-200	0	H_2O	0.00	0.00		0.00
	2.5		0.205	0.205		0.205
	5.0		0.395	0.40		0.405
	7.5		0.60	0.605		0.620
	10.0		0.80	0.805		0.83
			(Au lamp, 242.8 nm)			(247 nm^b)
Z-200	0	C_6H_{12}	0.00			0.00
	2.5		0.195			0.19
	5.0		0.38			0.38
	7.5		0.575			0.585
	10.0		0.76			0.785
			(Mg lamp, 285.2 nm)			(287 nm^b)
Phenol	0	NaOH 4.0 g l^{-1}	0.00			0.00
	10		0.275			0.27
	20		0.55			0.535
	30		0.82			0.815
			(Pt lamp, 270.2 nm)			(269 nm^b)
Phenol	0	HCl 20 ml l^{-1}	0.00			0.00
	10		0.16			0.15
	20		0.32			0.31
	30		0.48			0.46
	40		0.635			0.61
			(Pt lamp, 293.0 nm)			(292 nm^b)
Cresylic acid TD	0	NaOH 4.0 g l^{-1}	0.00			0.00
	10		0.23			0.22
	20		0.45			0.43
	30		0.665			0.65
	40		0.88			0.87

TABLE 1 (continued)

Reagent	Reagent concn. (mg l^{-1})	Solvent	Absorbance with a.a.s.			Absorbance with u.v. spectrometer
			Lamp 1[a]	Lamp 2[a]	Lamp 3[a]	
			(Mn lamp, 279.5 nm)			(277 nm[b])
Cresylic acid TD	0	HCl 20 ml l^{-1}	0.00			0.00
	10		0.12			0.11
	20		0.235			0.24
	30		0.345			0.36
	40		0.465			0.48
	50		0.58			0.61
	75		0.865			0.93

[a] Lamp currents and slit widths (spectral band-pass widths) used were those recommended by the manufacturer.
[b] Wavelength of absorption maximum (± 0.5 nm).

also be determined after extraction into chloroform [3], and results in Table 1 show that either a copper or silver lamp can be used in the a.a. unit for this determination.

Z-200 can be determined by u.v. spectrometry in aqueous solution [4] or after extraction into cyclohexane [4]. Results in Table 1 show that it can also be determined in these solutions with an a.a. spectrometer. The nearest convenient wavelength with the lamps available here was some 3 nm away from the absorption maximum; this resulted in slightly lower absorbance values than those obtained with the Unicam unit.

Absorbance measurements of solutions of the copper—dithiophosphate complex, phenol, and cresylic acid TD, obtained with the AA 1000 and the Unicam SP 800, are also listed in Table 1. Comparable absorbances were obtained for each solution with the two spectrometers, thus proving the validity of application of the a.a. unit to these reagents.

In plant solutions various interfering substances may be present. It has been shown [2—5] that most interferences can be overcome when a Unicam u.v.—visible spectrophotometer is used; the techniques involved are also applicable to an a.a. unit.

Selection of wavelength and lamp

Table 2 lists the main classes of flotation collector and two frothers together with the solvents commonly used in their determination and the wavelength of the absorption maximum in the solvent as determined with the Unicam SP800A. Table 2 also gives a selection of hollow-cathode lamps with suitable emission lines.

There are several ways of finding the wavelengths and lamps that can be used for absorbance measurements. Appropriate lamps emitting the desired wavelength (to within 2 nm) may be obtained by inspection of

TABLE 2

Recommended hollow-cathode lamps for determination of flotation reagents

Reagent	Solvent	Reagent λ_{max} (nm)	Recommended lamp	Wavelength of emission line (nm)
Dithiophosphate (copper complex)	Carbon tetrachloride	418	Ca	422.67
MBT	Chloroform	329	Ag	328.07
			Cu	327.40
	Water (pH $<$ 2)	323	Cu	324.75
			Li	323.26
	Water (pH $>$ 10)	310	Al	309.27
			Zn	307.59
Xanthate	Water	301	Fe	301.90
			Sn[a]	300.91
			Ni	300.25
Z-200	Cyclohexane	247	Cu[b]	249.21
			Fe	248.33
			Au	242.80
	Water	242	Cu	244.16
			Au	242.80
Phenol	Water (pH $>$ 11)	287	Mg	285.21
	Water (pH $<$ 6)	269	Pt	270.24
Cresylic acid TD	Water (pH $>$ 11)	292	Pt	292.98
	Water (pH $<$ 6)	277	Mn	279.48

[a] Application proved by B. S. Rawling (personal communication).
[b] Application proved by staff of Kanmantoo Mines Ltd. (personal communication).

manufacturers' lamp catalogues, although these catalogues do not list all the atomic lines emitted by a particular lamp but give only those suitable for a.a. determination of metals. For example, the nickel emission at 300.25 nm is useful for xanthate determinations, but is not nominated for nickel determinations by a.a.s. It may be desirable, therefore, to consult a handbook [10] or preferably a set of wavelength tables [11]. A lamp which has a strong line at the required wavelength should be selected.

Another method of seeking a suitable lamp and line is to use the a.a. unit to scan the emission spectrum of the lamps available. This spectrum will include the main lines of the element concerned and of the filler gas of the lamp.

Although it is desirable to seek a line close to the absorption maximum for maximum sensitivity, this is not absolutely essential for either routine or occasional measurements. For example, the mercury emission lines near 313 nm can be used [7] to measure xanthate residuals. A significant advantage of using an atomic line for absorbance measurements is that it obviates the need for wavelength calibration, as may be necessary with conventional spectrophotometers.

Instrumental

Although satisfactory results were obtained with the simple a.a. unit used, better precision should be obtainable with double-beam or higher quality instruments. Since absorbance measurements were made in the absence of the flame the meter readout was more stable than in conventional a.a.s.

Two other features of most a.a. spectrometers, which are not common on standard u.v.—visible spectrophotometers, are scale expansion up to 10 times and the ability to accommodate cells with 20-cm pathlength. These features should enable extremely low detection levels to be reached; this could be useful in work on effluents.

A disadvantage in using an a.a. spectrometer is that absorbance measurements are usually restricted to a maximum of 1.00. Hence concentrated solutions would require the use of cells with a shorter pathlength than 1 cm and/or dilution of the sample.

The system should be readily adaptable to continuous on-stream measurements if desired.

CONCLUSION

The results presented show that an a.a. spectrometer can be converted readily into an instrument capable of determining the absorbance of various reagents in aqueous and non-aqueous solvents in the visible and u.v. region. The technique enables a metallurgical analytical laboratory to extend its range of operations without additional cost.

Thanks are due to B. S. Rawling (The Zinc Corporation Ltd.) for suggesting the use of a tin lamp for xanthate determinations and to the staff of Kanmantoo Mines Ltd. for suggesting the use of a copper lamp for Z-200 determinations. J. V. Sullivan, CSIRO Division of Chemical Physics, provided many helpful comments.

REFERENCES

1 C. H. G. Bushell and M. Malnarich, Trans. AIME, 205 (1956) 734.

2 M. H. Jones and J. T. Woodcock, UV Spectrometry of Flotation Reagents with Special Reference to the Determination of Xanthate in Flotation Liquors, Institution of Mining and Metallurgy, London, 1973.

3 M. H. Jones and J. T. Woodcock, Can. Metall. Q., 12 (1973) 497.

4 M. H. Jones and J. T. Woodcock, Australas. Inst. Min. Metall. Proc., 231 (1969) 11.

5 M. H. Jones and J. T. Woodcock, Anal. Chem., 47 (1975) 11.

6 J. T. Woodcock and M. H. Jones, Australas. Inst. Min. Metall. Proc., 235 (1970) 76.

7 J. V. Sullivan and J. T. Woodcock, Australas. Inst. Min. Metall. Proc., 248 (1973) 1.

8 M. A. Hildon, Anal. Chem., 43 (1971) 973.

9 J. R. Edisbury, Practical Hints on Absorption Spectrometry, Hilger and Watts, London, 1966.

10 N. A. Lange (Ed.), Handbook of Chemistry, 10th edn., McGraw-Hill, New York, 1967, p. 959.

11 G. R. Harrison, Wavelength Tables, Massachusetts Institute of Technology, Cambridge, Mass., 1963.

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THE ENTHALPIMETRIC DETERMINATION OF MIXTURES OF CHLORIDE, BROMIDE AND IODIDE

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SUMMARY

The individual components of mixtures of chloride (0—1 mmol), bromide and iodide (0—0.1 mmol) may be determined by the use of direct injection enthalpimetry. The heats of reaction of the ions with various reagents have been shown to be additive and the use of non-selective reagents is thus made possible. The amounts of the halides present are calculated by simultaneous equations. The limits of the methods are discussed.

If in an equilibrium reaction of the type

$$aA + bB + c\mathrm{C} \rightleftharpoons b'\mathrm{B} + c\mathrm{C} + x\mathrm{X}$$

a sufficient excess of B (the titrant) is added to A (the analyte in a medium C), then provided the reaction velocity is greater than the rate of addition of B, the temperature change obtained, in adiabatic or quasi-adiabatic systems, may be used to determine the amount of A present. If the molar heat of reaction of A with B is ΔH, then the change in temperature (ΔT) in the system will be related to ΔH by $Q = C_s \Delta T = -\Delta H x$, or $\Delta T = -\Delta H x/C_s$, where Q is the total heat evolved or absorbed, C_s is the heat capacity of the system, and x is the number of moles of the product X formed. If the heat capacity of the system is kept practically constant, and the range of concentrations of A and the variations in ionic strengths are sufficiently small (i.e. ΔH will be constant), then we can write $\Delta T \equiv P \cdot x$, where P is the molar temperature pulse, i.e. the pulse per mole of product formed in the system under consideration ($\Delta H/C_s$).

The value of P will be particular to each analyte; thus, in a multicomponent system, comprised of say chloride, bromide and iodide in a reaction involving silver ions, P_{AgCl}, P_{AgBr} and P_{AgI} will have mutually independent values, which will be controlled only by the thermal characteristics of the system. In a reaction involving a mixture of analytes, the total temperature pulse will be the sum of all the partial temperature pulses of the components of the mixture. The partial temperature pulse of any analyte is that which

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would be obtained, by the reaction between reagent and the analyte, if that component alone occupied the whole sample volume. Thus

$$\Delta T \equiv \sum (aP_A + bP_B + cP_C + \ldots iP_I + P_M)$$

where a, b, c, . . . i represents the number of moles of analytes A, B, C, . . . I, having partial molar temperature pulses of P_A, P_B, P_C . . . P_I respectively, and P_M is the temperature pulse representing the dilution of the reagent. aP_A is the actual temperature pulse of A in the particular system.

The determination of a multicomponent system will require the use of as many reagents or system conditions as there are analytes present. Thus for the determination of the individual components of a mixture of chloride, bromide or iodide, it is necessary to use 3 separate systems, which vary either in the reagents used, or in the conditions of the medium.

In the work reported here, two reagents, silver ion, and chloramine-T (the sodium salt of *p*-toluene sulphochloramide) were used, the latter being used in two distinct pH conditions.

EXPERIMENTAL

Apparatus

The enthalpimetric titration system used has been described previously [1]. The sensitivity of the system was adjusted by alteration in the sensitivity of the recording potentiometer. The peripheral pipette used had a nominal capacity of 2 ml.

Determination of the partial temperature pulses

Solutions containing known amounts of the individual components were treated with the selected reagent under the appropriate conditions. The working volume in every case was 20 ml. The temperature pulses were recorded and, for each analyte, a calibration curve was obtained. The molar temperature pulse for the analyte was calculated from the slope of the calibration curve.

Silver ion titration (for chloride, bromide and iodide). The amounts of halide used per 20 ml of solution were between 0 and 1 mmol. The amount of 2.5 M silver nitrate solution in excess was not less than 2-fold in any titration. The results are given in Table 1.

Bromide and iodide. Chloramine-T reacts with both bromide and iodide, but not with chloride, at pH 2.5—3.5. The temperature pulses for bromide and iodide separately were determined for the range 0—0.1 mmol (Table 1). A saturated aqueous solution of (0.8 M) chloramine-T was used.

Iodide. At pH 8.0—9.0 only iodide reacts with chloramine-T. The temperature pulse for iodide was determined over the range 0—$1.5 \cdot 10^{-1}$ mmol (Table 1) with the 0.8 M solution of chloramine-T.

TABLE 1

Molar temperature pulses for systems used[a]

Reagent	Cl^-	Br^-	I^-
Ag^+	61	70	100
Chloramine-T			
(a) at pH 2.5	0	35	125
(b) at pH 8.5	0	0	40

[a] Amount of material, 0—0.15 mmol in a working volume of 20 ml.

Determination of mixtures. To aliquots of 10 ml of the mixture of halides were added 1—2 drops of 11 M HCl (for pH 2.5—3.5) or 5 ml of saturated sodium hydrogen carbonate solution and then water to bring the working volume to 20 ml. The aliquots were then treated with chloramine-T solution. A separate aliquot was acidified (pH 2) with nitric acid and treated with silver nitrate solution.

RESULTS AND DISCUSSION

It must be emphasized that the calculated "molar temperature pulses" are particular to the whole titration system; any alteration in the apparatus may bring about an alteration in the thermal capacity of the system and hence in the actual temperature change. This will be manifested as a change in the molar temperature pulse. Therefore the conditions established for the calibration and the determination of the pulses must be strictly adhered to in all assays. This applies especially to the maintaining of the temperature of the thermostat, for alteration in the temperature of the medium and of the reactants will change the resistance of the thermistor significantly, and although the bridge may be balanced, the overall sensitivity of the bridge, and therefore the molar temperature pulses, will change. During the present work, an electrical malfunction, external to the bridge and recorder system, resulted in the temperature of the thermostat rising by about 5 °C; the sensitivity of the bridge was noticeably different and different pulse values were obtained, so that recalibration was necessary.

The concentration ranges in the assay must be those used for the calibration, especially if the heat of dilution of the reactant has a significant value. For this investigation, the amount of silver nitrate used was reduced to that which would not give a noticeable (more than 1 %) variation in the heat of dilution when some silver had been removed by reaction.

Considering the dilution of the silver nitrate and the reaction of the halides with the silver nitrate, there are obviously two situations: (a) dilution may occur before the silver ions are removed as the insoluble halide, or (b) the silver reacts with the halide before it is solvated further. A comparison of results based on the two possibilities (a) and (b) showed that (a) was not completely valid; the values calculated on the assumption of dilution before reaction were generally within 1 % of the experimental values. The kinetics of the dilution reaction and those of the precipitation reaction need to be ascertained, to obtain a complete understanding of the temporal order of the reactions in the system. However, the error incurred, when one assumes that total dilution occurs before the reaction, seems to be acceptable; considering the requirements for nucleation and for the establishment of saturation equilibria, hypothesis (a) seems reasonable.

Analysis of the results

Calculations made on two series of binary and ternary mixtures showed that the error does not exceed ± 1.5 % and is generally less than 0.5 %. The standard deviation on a binary mixture is, as expected, less than that on a ternary mixture, being 0.2 % compared to 1.6 % for a total halide content of about 1 mmol.

The results are given in Tables 2—4; some are given in detail to indicate the type of reading obtained. The errors, obtained by calculation from one result at each assay condition, may be of the order of ± 2 % on the chloride,

TABLE 2

Results on synthetic mixtures of chloride, bromide and iodide

Halide taken (mmol)			Recorder reading				Corrected for dilution	Expected result
Cl^-	Br^-	I^-	1	2	3	Av.		
0	0	—	−16	−16	−16	−16	0	
0.1	1.0	—	75	74.5	75	75	91	91.5
0.2	0.8	—	66	65.5	66	66	82	82.2
0.4	0.6	—	63	63	63	63	79	82.4
0.6	0.4	—	62	62	62	62	78	78.5
0.8	0.2	—	60	60	59	60	76	76.8
1.0	0.1	—	65.5	66	66	66	82	82.4
0.2	0.2	0.2	40	40	41	40	56	55.8
0.4	0.4	0.4	95	93	94	94	110	111.6
0.6	0.6	0.6	150	150	148	149	165	167

TABLE 3

Errors for binary mixtures

	Mixture	Average deviation (%)	Maximum deviation
Ag^+	Cl^-/Br^-	0.6	1.0
	Cl^-/I^-	0.8	1.2
	Br^-/I^-	0.4	1.0
Chloramine-T, pH 2.5	Br^-/I^-	0.15	0.4
Chloramine-T, pH 8.5	Br^-/I^-	0.3	1.5

TABLE 4

Ternary mixtures

Actual value (mmol)			MTP[a]			Calculated value (mmol)		
Cl^-	Br^-	I^-	Ag^+	pH 2.5	pH 8.5	Cl	Br	I
0.20	0.40	0.60	100	89	24	0.20(5)	0.40	0.60
0.40	0.60	0.20	85	46	8	0.38	0.60	0.20
0.60	0.20	0.40	90	57	16	0.59(5)	0.20	0.40

[a] Each value is the average of 3 results differing by not more than 2 %.

which is the last value to be calculated and so accumulates errors from the previous calculations. Since in ternary systems chloride is always calculated from a system based on a reaction involving all three analytes as well as the maximum variation in the dilution effect, chloride values must be less accurate than those for iodide or bromide.

With 3 reaction vessels and titration pipettes, and one bridge and recorder system, the average time taken for 3 injections and the appropriate washings is about 2 min; the time taken for calculation is about 3 min (with non-automatic computation), thus within 5 min, it is possible to obtain an assay of the individual halides in a ternary mixture. If three results are required for each component, so that an average value may be obtained, it is necessary to have the reactants in the reaction vessel and to transfer the thermistor and stirrer from vessel to vessel. For a series of 9 titrations, the total time is then approximately 10 min. With suitable software, this time could be decreased to that required to dispense the solutions, allow thermal equilibrium of the system to be attained and then inject the reactants. With a suitably programmed calculator the process is completed within 5 min.

The process is not necessarily faster, more accurate or more precise than classical methods (including potentiometry), on "pure" mixtures. But for mixtures containing dyestuffs, as in colour photography, pharmaceutical intermediates and dyestuff manufacture, and/or surface-active reagents, it has the advantage that the sensor is not affected by colours, or surface-active reagents.

It is clear that the concept of molar temperature pulses is viable, and that for the enthalpimetric determination of mixtures it is not necessary to find a series of reactions which are selective to individual components of a multi-component mixture. Provided that the values obtained for the pulses are obtained under identical conditions to those used for assay purposes, at least 3 chemically similar species may be determined in admixture.

One of us (A. E. N.) thanks the University of Benin for sabbatical leave.

REFERENCE

1 L. S. Bark and J. K. Grime, Analyst (London), 97 (1972) 911.

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Short Communication

LOSS AND RECOVERY OF MERCURY FROM SEA WATER DURING STORAGE

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Care must be taken to prevent loss of mercury from aqueous solutions during sample storage [1—3]. In the case of sea water, acidification with mineral acids such as HNO_3 or HCl appears to be effective in reducing mercury losses. Coyne and Collins [4] have emphasized that nitric acid is effective only if the concentrated acid is present in the container before the sample solution is introduced. Fitzgerald et al. [5] pointed out that the preacidification method is unsuitable for polyethylene containers because spectral interference is caused by volatile organic matter leached by the concentrated acid; they recommended Pyrex or Teflon containers. Carr and Wilkniss [6], in their radioactive isotope study showed that at the time of sampling 80 % of the total mercury spiked in sea water was associated with particulates, while after 8-d storage at pH 1 (HNO_3), 10—15% was associated. Moreover, they suggested, though without quantitative data, that the flameless atomic absorption method was inadequate for the determination of mercury associated with particulate phases.

The work reported here was undertaken to establish if mercury losses are due to faults in the analytical procedure or to actual losses, when spiked sea water is stored in polyethylene containers.

Experimental

Apparatus. The Hitachi Model 508 atomic absorption spectrophotometer used was equipped with a mercury hollow-cathode lamp, and a gas cell with quartz windows (10-cm long, 9.1-cm^2 cross-section).

Reagents. All chemicals were of analytical grade. Redistilled water was used for reagent preparation. A 10% (w/v) tin(II) chloride solution was prepared with 1 M HCl as the diluent. The mercury blank of the 2 M HNO_3 stock solution was below 0.02 p.p.b. The standard mercury stock solution

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(1.0798 g of red HgO dissolved in 1 l of 1 M HNO_3) was diluted weekly with HNO_3 and water to give a 1-p.p.m. intermediate standard solution (0.1 M HNO_3). Working standards (0.4 p.p.m.) were prepared daily by diluting the intermediate solution with water.

Sample containers and sample preparation. Screw-cap 1-l polyethylene bottles were used as sample containers. The bottles were scrubbled with soap and water, stored overnight in HNO_3 (ca. 1 M), rinsed with distilled water, and dried in an oven. Sea-water samples were collected at the surface in Shimabara Bay off Amakusa Islands in Kumamoto Prefecture. Suitable volumes of the unfiltered sample solutions were transferred to the polyethylene bottles and acidified with 2 M HNO_3 to various concentrations to yield final volumes of 1 l. Then, the solutions were spiked with 1 ml of 1-p.p.m. Hg standard to give a 1 p.p.b. concentration. In the recovery studies, acidification with nitric acid was done after the spiking.

Measurements. All measurements were carried out by the cold-vapor atomic absorption technique with a closed system. To a 300-ml gas bubbler were added distilled water (50 ml), 1 + 1 H_2SO_4 (2 ml), and $SnCl_2$ solution (2 ml); the mixture was then aerated to remove any mercury arising from the reagents. An aliquot (100 ml) of the sample solution was then added to the bottle, and the absorption peak of mercury vapor recorded. The quantity of mercury was determined by means of a calibration curve prepared with each set of samples. The detection limit was 0.02 p.p.b.

Results and discussion

The changes with time in the mercury concentrations in the spiked solutions at various acidities are shown in Table 1. Acid concentrations above 0.1 M were effective in preventing mercury losses for a period of at least 4 months; with 0.01 M acid, a steady decrease in mercury concentration with time was observed after 20 d. When the solutions were not acidified or contained only 0.001 M acid, the mercury losses were essentially complete within 5 d. However, after a spiked sample had been allowed to stand for 5—10 d without acidification, and HNO_3 was then added to yield a 0.1 M concentration, quantitative recoveries were found after 10 d (Table 1). The data seem to indicate that "loss" of mercury from sea water during storage does not mean disappearance, but conversion to a state that cannot be measured by the atomic absorption method. Some workers [7, 8] have pointed out that, in natural water analysis, reduction of mercury with reducing agents is incomplete; they ascribed this to the formation of mercury complexes with naturally occurring chelating agents. However, the present results appear to support the opinions of Carr and Wilkniss [6], who reported that the flameless atomic absorption method could not give a meaningful analysis for total mercury if the major fraction of the element was associated with particulate phases. When the sample is acidified, the mercury strongly adsorbed on suspended colloids, solid particles, and container walls, may be released into the aqueous phase or converted to readily reducible states. The quite favorable stability of mercury in the more strongly acidified sea water

TABLE 1

Changes with time in mercury concentrations of spiked sea water during storage

Acidity (M)	Hg (p.p.b.)/Standing time[a]					
Loss of Hg at various HNO_3 concentrations						
None	0.98/5m	0.57/20h	0.34/2d	0.11/3d	0.04/4d	n.d.[b]/5d
0.001	1.00/1h	0.60/20h	0.18/2d	0.10/3d	n.d./5d	
0.01	1.04/1h	1.08/2d	0.98/6d	1.10/10d	1.08/20d	0.96/30d
	0.86/40d	0.30/60d				
0.1	1.02/1h	1.08/1d	1.08/4d	1.08/10d	1.10/20d	1.10/40d
	1.10/60d	1.12/120d	1.30/270d			
0.5	1.08/2d	1.10/10d	1.02/20d	1.10/40d	1.08/60d	1.10/160d
	1.22/270d					
Recovery of Hg from unacidified sample						
0.1	n.d./1h	0.30/1d	0.82/2d	0.92/4d	0.98/6d	1.02/10d
	1.02/20d	1.04/60d				

[a] Signs m, h and d mean minutes, hours and days, respectively.
[b] n.d. means below the detection limit (0.02 p.p.b.).

during long-term storage may be due to the chloride present, since acidifying distilled water with nitric acid seems much less effective [3]. Stable chloro—mercury complexes ($HgCl_3^-$ and $HgCl_4^{2-}$) may inhibit resorption by solid phase

In contrast to mercury losses, Bothner and Robertson [9] have recently reported that sea-water samples, acidified and stored in polyethylene bottles, can increase in mercury concentration with time because of contamination from airborne vapor. Such a remarkable increment of mercury as they reported was not observed in the present work, possibly because of the different surroundings in the two laboratories. However, during long-term experiments under stable storage conditions, 10—20% increments in the spiked mercury amounts were observed after 9 months (Table 1). This may be due to accumulation of airborne mercury diffusing through polyethylene container walls. It should be emphasized that care must be taken. If the atmosphere contains 1 μg Hg m^{-3}, which is not unusual for laboratory air, the solubility of mercury vapor in water has been estimated to be 0.0034 $\mu g\ l^{-1}$ at 20°C [10].

REFERENCES

1 R. W. Rosain and C. M. Wai, Anal. Chim. Acta, 65 (1973) 279.
2 Y. Dokiya, S. Yamazaki and K. Fuwa, Environ. Lett., 7 (1974) 67.
3 C. Feldman, Anal. Chem., 46 (1974) 99.
4 R. V. Coyne and J. A. Collins, Anal. Chem., 44 (1972) 1093.
5 W. F. Fitzgerald, W. B. Lyons and C. D. Hunt, Anal. Chem., 46 (1974) 1882.
6 R. A. Carr and P. E. Wilkniss, Environ. Sci. Technol., 7 (1973) 62.
7 R. J. Baltisberger and C. L. Knudson, Anal. Chim. Acta, 73 (1974) 265.
8 L. Lopez-Escobar and D. N. Hume, Anal. Lett., 56 (1973) 378.
9 M. H. Bothner and D. E. Robertson, Anal. Chem., 47 (1975) 592.
10 I. Sanemasa, Bull. Chem. Soc. Jpn, 48 (1975) 1795.

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Short Communication

ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF SOME TRACE METALS IN FISH MEAL AND BOVINE LIVER BY THE SOLID SAMPLING TECHNIQUE

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The universal interest in the occurrence, distribution and toxic effects of trace elements has initiated many studies of their levels in biological materials. The trace metals are frequently determined by atomic absorption spectrometry (a.a.s.). A common procedure is to decompose the organic matrix by dry or wet ashing, and to determine the metals by atomization, either in the flame or in a furnace. The solid sampling technique in a.a.s. offers some definite advantages in the analysis of biological materials; up to the present time these advantages have been utilized by only a few authors [1—7].

The present communication describes the determination of cadmium, copper, lead and manganese in four samples of Norwegian fish meal and in the NBS (SRM 1577) bovine liver. The analyses were made by atomizing the metals either from the original solid materials, or from dry-ashed samples. For comparison, the samples were also decomposed by wet ashing, and the elements were determined by atomization in the flame.

Experimental

Apparatus. Perkin-Elmer 303 and 400 S atomic absorption spectrophotometers were used; both instruments were equipped with arc source deuterium lamps for background correction, and the 400 S spectrophotometer had also a tungsten lamp for corrections in the range 300—800 nm.

Solid samples were atomized in a graphite furnace, the construction of which has been described elsewhere [8]. These analyses were done with the 303 instrument and were based on measuring peak areas. Liquid samples were atomized in the flame with the 400 S photometer and the proper background corrector.

Samples were ground in agate mortars and pestles. Weighings were made with semi-micro or micro balances.

Samples. The fish meal samples were industrial products of mackerel, blue whiting, capelin and hexane-extracted capelin. The samples had been dried by steam, and no conserving agents had been added. The main constituents of the former three products were: protein, about 72 %; water, about 7 %;

ash, about 12 %; sodium chloride, about 1.7 %; and fat (Soxhlet), about 9 %. In the hexane-extracted capelin, the protein content was about 80 %, and the fat content (Soxhlet) about 0.7 %. The samples were relatively coarse powders in which tissue fibers and particles of bone could be seen with a magnifying glass. The samples of fish meal were not dried before analysis.

The bovine liver was stored in a refrigerator at about 4 °C; before analysis portions were dried by lyophilization as prescribed by NBS.

Reagents and standard solutions. Standard solutions of the four elements were prepared by dissolving the appropriate amounts of high-purity metals in a small excess of nitric acid. In all diluted standard solutions, the pH was maintained at or below 2.0 by adding, where required, nitric acid.

The acids were of Suprapur quality (E. Merck). The furnace was purged with argon (purity 99.9 %, by volume).

The hydrogen peroxide solution (30 %) was reagent grade.

Sample preparations. About 5 g of the fish meal samples were transferred to platinum dishes and charred at 450 °C in an electric furnace. The residues were mixed intimately by grinding in an agate mortar and pestle, to pass a 270-mesh sieve. This ashing step concentrated the trace elements by about 10 times.

Because of the risk of losing cadmium during dry ashing, portions for analysis by direct atomization were taken from the original materials, which were ground to pass a 200-mesh sieve.

The bovine liver was not ashed; portions were ground to pass a 270-mesh sieve.

The five samples were also decomposed by wet ashing, 5-g portions being attacked with nitric acid and hydrogen peroxide solution. The samples and a blank solution were finally diluted to 50 ml with water.

Procedure. Before the start of the measurements, the hollow-cathode and background corrector lamps were heated for about 15 min. The flow of argon through the graphite furnace was adjusted to 0.36 l min^{-1}. The wavelengths for the measurements are listed in Table 1. The operating conditions for the graphite furnace were as follows: a) drying for 30 s at 100 °C in all cases; b) ashing for 60 s at 350 °C for Cd and at 450 °C for Cu, Pb, Mn; c) atomization for 30 s at 1700 °C for Cd and at 1950 °C for Cu, Pb, Mn; d) cleaning at 1950 °C in all cases.

Of the solid original or pre-ashed samples 0.3—6 mg was weighed in small tantalum scoops and placed in the middle of the furnace by means of a specially constructed adjustable inserting device. The scoops were reweighed

TABLE 1

Wavelengths for measurement

Metal	Cd	Cu	Pb	Mn
λ (nm)	228.0	327.4	217.0 or 283.3	279.5 or 403.1

TABLE 2

Analytical results for cadmium, copper, lead and manganese in NBS (SRM-1577) bovine liver and fish meals (All contents as p.p.m.)

Element	Solid sampling				Flame atomization	
	St. add. curve I		St. add. curve II			
	$\bar{X}$[a]	s_r[b]	$\bar{X}$	s_r	$\bar{X}$	s_r
Bovine liver[c]						
Cd	0.30	8	0.32	13	0.30	7
Cu	196	6	192	9	208	11
Pb	0.36	12	0.35	22	0.33	7
Mn	10.5	16	10.8	20	10.0	5
Fish meal (mackerel)						
Cd	0.29	13	0.26	19	0.28	7
Cu	3.9	30	3.5	20	4.0	7
Pb	1.1	23	1.3	21	1.0	10
Mn	2.1	13	1.9	16	1.9	6
Fish meal (blue whiting)						
Cd	0.15	30	0.13	19	0.15	6
Cu	3.6	6	3.4	9	3.8	5
Pb	1.4	8	1.5	10	1.3	8
Mn	8.0	17	8.5	25	8.5	8
Fish meal (capelin)						
Cd	0.35	17	0.40	18	0.40	10
Cu	4.3	13	4.3	7	4.5	7
Pb	1.0	12	1.1	18	0.90	10
Mn	2.4	25	2.2	22	2.2	6
Hexane-extracted fish meal (capelin)						
Cd	0.17	17	0.20	15	0.17	6
Cu	4.9	9	5.0	6	4.8	12
Pb	0.60	11	0.70	13	0.60	5
Mn	2.2	14	2.3	13	2.7	17

[a] $\bar{X}$, average p.p.m.; [b] s_r, relative standard deviation. [c] Certificate values: 0.27 ± 0.04 p.p.m. Cd; 193 ± 10 p.p.m. Cu; 0.34 ± 0.08 p.p.m. Pb; 10.3 ± 1.0 p.p.m. Mn.

and the furnace was moved to its preadjusted position. Two portions of the sample were atomized without addition of standard solution; to three or four portions 5—20 μl of metal standard solution were added. From the integrated absorption data, the position of the standard addition curve, the intercept on the abscissa and the standard deviation of the value found were derived by the method of least squares. Two standard addition curves were plotted for each metal.

The analyses of the sample solutions were also based on the use of standard addition. From the 50-ml sample solutions four 4-ml portions (for the determination of copper in bovine liver, 1-ml portions were taken) were transferred to sample bottles. To one of the bottles 1 ml of water was added, to the others 1 ml of metal solution of varying appropriate concentrations were added (in the analysis for copper in bovine liver 4 ml of water and 4 ml of 30, 60 and 90 p.p.m. copper standard solution were introduced). The series of solutions and blanks were atomized in the air—acetylene flame, and the averages and the relative standard deviations were calculated from the resulting standard addition curve.

Results

Analytical data from determinations of cadmium, copper, lead and manganese in the four fish meal samples and in the NBS (SRM-1577) bovine liver are listed in Table 2, which also includes the data from the NBS provisional certificate. The present data for bovine liver are in good agreement with the certificate values; consequently, serious systematic errors should not be present. For the other samples no data on the content of the trace metals were available. The agreement between values obtained by solid sampling and by atomization of liquid samples in the flame is satisfactory.

The precision (given as relative standard deviation) of the solid sampling technique ranges from 6 to 30 %; these values have to be considered as normal at the concentration levels present. In the four fish meal samples the contents (in p.p.m.) of the metals ranged as follows: cadmium 0.13—0.40; copper 3.4—5.0; lead 0.60—1.5 and manganese 1.9—8.5.

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REFERENCES

1 W. B. Barnett and H. C. Kahn, Clin. Chem., 18 (1972) 923.
2 D. A. Church, T. Hadeishi, L. Leong, R. D. McLaughlin and B. D. Zak, Anal. Chem., 46 (1974) 1352.
3 G. Lundgren and G. Johansson, Talanta, 21 (1974) 257.
4 F. J. Langmyhr and A. Sundli, Anal. Chim. Acta, 73 (1974) 81.
5 Y. J. Belyaev and V. V. Gordeev, Okeanologiya, 12 (1972) 905.
6 C. J. Pickford and G. Rossi, At. Absorpt. Newslett., 14 (1975) 78.
7 F. J. Langmyhr and T. P. Lind, Anal. Chim. Acta, 80 (1975) 297.
8 F. J. Langmyhr and Y. Thomassen, Z. Anal. Chem., 264 (1973) 122.

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Short Communication

COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF NANOGRAM AMOUNTS OF ORGANIC MERCURY IN SEDIMENTS OR AQUATIC ORGANISMS

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Although methylmercury has been found in aquatic organisms, its origin is not clearly known. It is generally assumed that methylmercury exists in natural waters and that the organisms concentrate it, because it has been detected in many aquatic organisms; also the methylation of inorganic mercury in sediments has been reported by several investigators [1—3].

A cold-vapor atomic absorption spectrometric method for the determination of organic mercury has been reported by Bisogni and Lawrence [4]. The method consists of the extraction of organic mercury with benzene, back-extraction with cysteine, decomposition of cysteine, which interferes with the tin(II) reduction of organic mercury, by treatment with potassium permanganate—potassium persulfate, and determination of the inorganic mercury produced, as described by Hatch and Ott [5]. Generally, a complicated procedure of this type should be avoided because of possible contamination in the determination of nanogram amounts of elements.

As Umezaki and Iwamoto [6] have reported that organic mercury can be reduced directly with tin(II) chloride in the presence of sodium hydroxide and copper(II), the determination of organic mercury can be simplified, particularly if the reagent used for back-extraction does not interfere with the reduction of organic mercury. Back-extraction with an ammoniacal glutathione solution was found to be satisfactory.

In the method proposed, contamination only from the ammoniacal glutathione solution is expected. However, any inorganic mercury in this solution will be adsorbed on the glass container walls with a half-life about 2 d, i.e., the blank value becomes zero if the solution is left to stand for more than a week.

Mercury in sediments or aquatic organisms found in unpolluted waters is inorganic and methylmercury; no ethyl- or phenyl-mercury has been reported. The identification of the type of organic mercury is impossible by the proposed method, and it is assumed that organic mercury in natural environments is present as monomethylmercury.

Experimental

Apparatus. A Jarrell-Ash Model AA-780 atomic absorption spectrometer was used with a quartz tube (1.5-cm diam., 20-cm long).

Procedure. Use ionized or distilled water preserved in a polyethylene or glass bottle for more than a week.

To 10—20 g of sediment or 0.5—1 g of aquatic organism, add 10 ml of 2 M hydrochloric acid, and leave for 2 days [7]. Filter the samples through a glass filter, and wash with 10 ml of 2 M hydrochloric acid. Extract organic mercury from 20 ml of the filtrate into 40 ml of benzene by shaking for 3 min, and discard the aqueous layer. Add 20 ml of $3 \cdot 10^{-4}$ % glutathione in 0.1 M ammonia solution, and back-extract organic mercury into the aqueous solution by shaking for 2 min.

To a gas washing bottle, add 150 ml of water, 10 ml of 10 M sodium hydroxide, 2 ml of 1000 p.p.m. copper solution and 5 ml of 5 % tin(II) chloride dihydrate solution. Pass nitrogen gas at a flow rate of 1.4 l min^{-1} for 6 min to eliminate any mercury in the reagent solutions. Then add the aqueous back-extract from the sample. Concentrate [8] the mercury on 1.5 g of gold granules (about 1-mm diameter) packed in a glass tube (4-mm i.d.) by passing nitrogen gas for 6 min. Heat the gold granules in a boat to 500 °C in a furnace for 2 min, and measure the absorbance at 253.7 nm by passing nitrogen gas at a flow rate of 1.2 l min^{-1}.

Results and discussion

The optimal conditions were investigated with 50 ng of methylmercury added to 20 ml of 2 M hydrochloric acid. The extraction rate from the aqueous layer was calculated by determining the methylmercury remaining in the aqueous layer after the extraction; 95 % extraction was obtained with a single extraction. Glutathione concentrations in the range $1—5 \cdot 10^{-4}$ % in 0.1 M ammonia solution, and ammonia concentrations in the range 0.07—0.2 M in $3 \cdot 10^{-4}$ % glutathione solution, gave constant maximal recoveries. Shaking for more than 2 min in the extraction and more than 1 min in the stripping step sufficed. Glutathione, even as the solid, is gradually oxidized by atmospheric oxygen, so that its activity decreases with time. If low recoveries of methylmercury were obtained, higher glutathione concentrations, which interfered in the reduction of methylmercury were needed. However, the ammoniacal glutathione solutions were stable for at least a month at room temperature; ammonia seems to prevent the oxidation of glutathione, but the mechanism is not clear.

In the recommended method, the relative standard deviations were 4.1 and 10.2 % at the 50 and 5 ng absolute level of methylmercury(II) added to 20 ml of 2 M hydrochloric acid. The final recovery of methylmercury was 86 %.

This method was applied to the determination of organic mercury in unpolluted sediments and rockfish. Organic mercury in two sediment samples was 0.22 ± 0.03 and 0.43 ± 0.03 ng Hg g^{-1} (dry weight). Andren and Harris [9] have reported a methylmercury concentration of 0.02 — 0.1 ng Hg g^{-1} in unpolluted sediments by using a gas chromatograph with an electron capture detector. In two rockfish samples, the organic mercury concentration was 0.11 ± 0.01 and 0.19 ± 0.01 p.p.m. (dry weight); this agrees quite well with the reported methylmercury concentration range of 0.07—0.20 p.p.m. Hg in similar fish [10]. From those results, the present data are assumed to correspond to methylmercury.

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REFERENCES

1 S. Jensen and A. Jernelov, Nature (London), 223 (1969) 753.
2 A. Jernelov, Limnol. Oceanogr., 15 (1970) 958.
3 D. G. Langley, J. Water Pollut. Control Fed., 45 (1973) 44.
4 J. J. Bisogni, Jr. and A. W. Lawrence, Environ. Sci. Technol., 8 (1974) 850.
5 W. R. Hatch and W. L. Ott, Anal. Chem., 40 (1968) 2085.
6 Y. Umezaki and K. Iwamoto, Jpn. Anal., 20 (1971) 173.
7 K. Irukayama, M. Fujiki, S. Tajima and S. Omori, Jpn. J. Public Health, 19 (1972) 25.
8 M. Nishimura, K. Matsunaga and S. Konishi, Jpn. Anal., 24 (1975) 655.
9 A. W. Andren and R. C. Harris, Nature (London), 245 (1973) 256.
10 T. Amemiya, M. Takeuchi, K. Ito, K. Ebara, H. Harada and T. Totani, Ann. Rep. Tokyo Metropolitan Res. Lab. Public Health, 26-1 (1975) 129.

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Short Communication

THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH 8-HYDROXYQUINOLINE

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A simple rapid determination of uranium in the presence of many other metals was required for studies of the recovery of uranium from sea water by passage of large volumes through chelating ion-exchange columns. The spectrophotometric methods based on 8-hydroxyquinoline in the presence of EDTA [1] and on 4-(2-pyridylazo)-resorcinol (PAR) [2] were chosen for examination. The uranium content of sea water is 0.003 p.p.m. [3]; as many other metals are present at about this level, prior separation is essential. The extraction of uranium from sulphate solution by amines has been studied in various separation schemes [4–6]. Rusheed et al. [6] examined the separation of uranium and vanadium in the pH range 1–2, and reported that lowering the pH favours uranium extraction. Consequently, extraction of uranium from sulphate solution at pH 0.85 by trioctylamine [7] was selected for the extraction step.

After back-extraction with nitric acid, the uranium was determined with 8-hydroxyquinoline; to check the results, the chloroform extract of the uranium–8-hydroxyquinolinate was wet-ashed, and the uranium was determined by the PAR method.

Experimental

Chemicals and equipment. Reagent-grade chemicals were used; the tri-n-octylamine (R. N. Emanuel) was 97 %. A Cecil Instruments CE 272 spectrophotometer and a Pye model 291 pH meter with combined electrode assembly were used.

Procedure. Take an aliquot of sample containing 250 μg of uranium and dilute to about 50 ml with deionized water. Adjust the pH to 0.85 with sulphuric acid, and transfer the solution to a 250-ml separating funnel. Extract the uranium by shaking for at least 1 min with two 25-ml portions of 0.1 M trioctylamine solution in (60–80) petroleum ether containing 2 % (v/v) octan-2-ol. Back-extract the uranium with two 25-ml aliquots of 0.2 M nitric acid. Neutralize the nitric acid with ammonia solution, finally adjusting to pH 8.8. Add 5 ml of 0.02 M EDTA (disodium salt) and extract with two

10-ml aliquots of 1 % (w/v) 8-hydroxyquinoline solution in chloroform. Determine the absorbance of the chloroform solution in a 1-cm cell at 400 nm against a reagent blank.

The molar absorptivity of the method is about 17 400 l mol^{-1} cm^{-1}, and the linear response range was 0—275 μg of uranium.

Results and discussion

Interference studies. In the first series of tests, 500 μg of uranium were mixed with eight other metals in the ratios in which they are present in sea water; thus, the solutions contained 500 μg each of vanadium, molybdenum, copper, nickel and manganese, 1000 μg each of zinc and iron, and 100 μg of cobalt. Application of the above procedure to aliquots showed that the uranium recoveries were quantitative.

When the chloroform extract was wet-ashed and the uranium content determined by the PAR method, again quantitative recoveries were obtained, proving that the absorbance measured in the 8-hydroxyquinoline method is due to the uranium complex and not to complexes of other metals which might have passed through the extraction procedure.

Crouse and Brown [7] have stated that molybdenum(VI) will be extracted into trioctylamine and vanadium(V) will be extracted if molybdenum is present. According to Taylor [1], titanium is extracted from EDTA solution under the same conditions as uranium. The effects of zirconium on the extraction or colorimetric determination have not been described.

In the second series of interference studies, nineteen metals were examined at concentrations 50 times greater than the uranium concentration. Thus 200 μg of uranium was determined from a solution containing 10 mg of each of the following: Al, As, Bi, Cd, Ce, Co, Cr, Fe, Pb, Mn, Ni, Mo, Sn, Ti, V, W, Zn and Zr. Again the recovery of uranium was quantitative. Uranium recoveries in the presence of large amounts of sodium, potassium, ammonium, calcium and magnesium salts were also quantitative.

The presence of much nitrate or chloride in the initial solution interfered with the uranium extraction. If these anions are present in excessive amounts, they must be removed by adding sulphuric acid to the sample aliquot and heating to fumes.

Typical results for uranium determinations are given in Table 1.

Although the PAR method for uranium exhibits greater sensitivity and in the first series of interference studies reproducible quantitative recoveries of uranium were noted, the PAR method proved to be unreliable. In sea-water determinations, and even in the standard uranium solutions, different intensities of colour were found with the PAR reagent which appears to be sensitive to the concentration of ammonium salts present. In a large number of determinations, the 8-hydroxyquinoline method preceded by the amine extraction step, has given reliable and reproducible results.

TABLE 1

Typical uranium analyses in the presence of other metal salts

Sample solution	Uranium recovery (%)
(1) 500 μg U	100.0
(2) 500 μg (each) U, V, Mo, Cu, Ni, Mn; 1 mg (each) Fe, Zn; 10 μg Co	96.9 (by oxine) 100.0 (by PAR)
(3) 200 μg U	98.7
(4) 10 mg (each) Al, As, Bi, Cd, Ce, Co, Cu, Cr, Fe, Pb, Mn, Ni, Mo, Sn, Ti, W, V, Zn, Zr	0
(5) As (4) + 200 μg U	101.3

REFERENCES

1 R. P. Taylor, Ph.D. Thesis, Princeton University, 1954.
2 F. H. Pollard, P. Hanson and W. J. Geary, Anal. Chim. Acta, 20 (1959) 26.
3 T. F. Gaskell, Chem. Ind. (London), 41 (1971) 1149.
4 K. B. Brown, C. F. Colman, D. J. Crouse and J. G. Moore, USAEC, Report AECD — 4142 (1954).
5 K. B. Brown, C. F. Colman, D. J. Crouse and A. D. Ryan, Report ORNL — 2443 (1957).
6 A. Rusheed, A. H. Qazi, S. Ahmad and M. Ashraf, Sep. Sci., 10 (1975) 507.
7 D. J. Crouse and K. B. Brown, Report ORNL — 1959 (1956).

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Short Communication

THE PROPERTIES OF POLY(VINYL ISOBUTYL ETHER) AS A MATRIX FOR ION-SELECTIVE ELECTRODES

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It is well-known that liquid-membrane ion-selective electrodes suffer from some disadvantages compared with solid-state membrane electrodes. Their response is disturbed by hydrostatic pressure, stirring, and surface-active agents and they require greater skill and care for reliable use. These difficulties have been overcome by introducing ion-selective electrodes based on a homogeneous matrix (sometimes classified as solid ion-exchange electrodes) which exhibit greatly improved working characteristics and thus are an excellent alternative to the liquid-membrane electrodes.

Whilst the number of ion-exchangers and neutral sequestering agents examined is considerable, the field of matrix materials is virtually unexplored. This is undoubtedly because the most frequently used material — plasticized poly(vinyl chloride) (PVC) — provides a convenient matrix with satisfactory properties [1]. It should be emphasized that the solvent or the matrix material of an ion-selective electrode influences the selectivity pattern considerably. For example, the calcium-selective electrode developed by Schultz et al. [2], in which the calcium salt of a dialkylphosphoric acid is incorporated in collodion, is less sensitive to hydrogen ions and more sensitive to sodium ions than the classical liquid-membrane electrode developed by Ross [3]. Therefore, it might be possible to promote a desired selectivity by the choice of an appropriate matrix material. The question as to whether matrix materials can be found which need no addition of plasticizers or mediators also deserves attention. (Since plasticizers facilitate charge transport by lowering the glass transition temperature of a polymer, the function of mediators is ascribed to their solvating properties [4, 5].)

This communication reports a preliminary study of poly(vinyl isobutyl ether), which is a plasticized polymer in its own right because of its bulky isobutyl groups, as a matrix material for ion-selective electrodes.

Experimental

Chemicals. Poly(vinyl isobutyl ether) was the commercial product Lutonal IC (BASF, Germany). Membranes were made from a highly viscous material (Lutonal IC; *K* value, 64.9; abbreviated as Lutonal-64.9) and from a material displaying elastic and plastic properties (Lutonal IC; *K* value, 110; abbreviated as Lutonal-110). The *K* value, characterizing the viscosity behaviour of the polymer, is related to the molecular weight.

Calcium bis(di-2-ethylhexylphosphate) [$Ca(DEHP)_2$] was prepared as described by Cattrall et al. [6]. Other ion-exchangers or neutral carriers used were thenoyltrifluoroacetone (Merck), valinomycin (Serva, Germany), and methyltricaprylylammonium chloride (Adogen-464, Aldrich Chemical Company).

Membrane preparation. Membranes based on Lutonal-110 without added plasticizers or mediators were made as described by Moody et al. [1] by pouring a solution of the membrane components on plate glass and allowing the solvent to evaporate. This method was not practicable in other cases. Since the membranes containing plasticizers or mediators were very flexible and membranes from Lutonal-64.9 were adhesive, they could not be peeled away from the glass without distortion. These membranes were therefore made by repeatedly applying a solution of the membrane components in small amounts to glass fibre paper (Whatman GF/A) resting on a glass ring, and allowing the solvent to evaporate between applications. The thickness of all membranes was about 0.8 mm.

Electrode assembly and e.m.f. measurements. The membranes were clamped between the two symmetrical halves of a Plexiglas flow-through cell [7]. This cell allowed convenient and frequent change of the solutions on both sides of the membrane, and contamination of the solutions by KCl from the two calomel electrodes was avoided. E.m.f. was measured at 25°C with a Radiometer pH Meter 4 (input impedance, 10^{12} ohm).

Ion activities were calculated by the Kielland method [8]. Selectivity factors were determined by the separate solution method in 10^{-2} M chloride solutions by means of the extended Nikolsky equation.

Results and discussion

The first membranes were made from 10% (w/w) solutions of pure Lutonal-64.9 and Lutonal-110 in ethyl acetate. The Lutonal-110 membranes gave no response in 10^{-2} M KCl solution for several months, but the Lutonal-64.9 membranes became permeable after 4 d. This result is not surprising as low-molecular-weight Lutonals are soluble in water. This behaviour, and the observation that both membranes became opaque on exposure to water, indicate that with Lutonal-110 membranes — in contrast to Lutonal-64.9 membranes — the swelling is restricted to the surface layer.

The performance of membranes made from Lutonal-110 and $Ca(DEHP)_2$ or Adogen-464 without any plasticizer or mediator has been investigated by Vogel [9]; these membranes functioned neither satisfactorily nor reproducibly. In some cases, membranes containing 10% $Ca(DEHP)_2$ obeyed the Nernst equation, but their lifetime was less than one month and they exhibited time-dependent asymmetry potentials. Membranes with high contents of Adogen-464 (30—50%) needed no soaking before use and gave fast responses. Clearly, the active material functioned simultaneously as a plasticizer, like *N,N*-dimethyloleamide in PVC membranes [10]. However, the membranes incorporating Adogen-464 displayed sub-Nernstian behaviour, and an Adogen exudate appeared on the membrane surface.

Because the membranes with pure Lutonal-110 as matrix gave poor electrode responses, attempts were made to improve their properties by addition of decan-1-ol, which seems to be the most promising mediator for calcium sensors [5]. Decanol is compatible with Lutonal-110, and the maximum decanol content of 40% proved to be consistent with satisfactory mechanical properties when a supporting material was used. Table 1 summarizes the composition and properties of various membranes containing decanol. The best results were obtained with the calcium sensor. The electrodes had a long life and rapid response, and needed either no soaking or only overnight soaking before use. The selectivity pattern of electrode II (Table 2) is similar to that of an electrode based on $Ca(DEHP)_2$, PVC, and decanol reported by Craggs et al. [5]. The electrode does not discriminate between calcium and

TABLE 1

Composition and characteristics of ion-selective homogeneous-matrix membrane electrodes based on poly(vinyl isobutyl ether)
(Solutions of 10% Lutonal-110 in appropriate solvents were used: $Ca(DEHP)_2$, ether—propan-1-ol in a 1 : 1 (w/w) mixture; Adogen or thenoyltrifluoroacetone, ethyl acetate; valinomycin, n-hexane.)

Electrode number	Active component	Composition (% weight)			Properties
		A[a]	D	L	
I	$Ca(DEHP)_2$	10	30	60	Overnight soaking needed. Slope, 30 mV/decade (10^{-1}—10^{-4} M). Response time, 0.5 min. Lifetime, several months.
II	$Ca(DEHP)_2$	10	40	50	No soaking required. Slope, 30 mV/decade (10^{-1}—10^{-4} M). Response time, seconds. Lifetime, several months. Selectivity: see Table 2.
III	Adogen-464	5	30	65	Weak Adogen exudate.[b]
IV	Adogen-464	1	30	69	No Adogen exudate.[b]
V	Thenoyltrifluoroacetone	5	30	65	High time-dependent asymmetry potentials (10—30 mV) in 10^{-2} M $CaCl_2$ solutions.
VI	Valinomycin	4	35	61	Very slow response. Sensitive to rinsing.

[a] A = active component. D = decanol. L = Lutonal.

[b] For these electrodes, no soaking was needed, but responses were sub-Nernstian and time-dependent.

TABLE 2

Selectivity factors for calcium-selective electrodes with decanol as mediator

	Mg^{2+}	Sr^{2+}	Ba^{2+}	H^+	Na^+	K^+
This study	≈1	0.5	0.3	10^3—10^4	1.3	1.3
Craggs et al.	1	0.5	0.5		2.4	2.4

magnesium and therefore behaves like the classical liquid-membrane water hardness electrode composed of a calcium sensor and decanol. The observation [9] that plasticizers do not enhance the electrode quality of Lutonal-110 membranes containing $Ca(DEHP)_2$, indicates that decanol in these electrodes exhibits predominantly mediator functions.

Even though the calcium electrode described shows only a moderate hydrogen interference, it should not be exposed to solutions of pH less than about 3.5. Otherwise, both the slope factor and the sodium interference increase, and the electrode cannot then be restored to normal operation. This finding is in accord with that of Griffiths et al. [11].

As can be seen from Table 1, satisfactorily working electrodes with Adogen-464 and decanol could not be obtained. Interestingly, electrodes with only 1 % active material gave a fast response; without decanol, there was no response at low Adogen-464 concentrations. However, it should be possible to find high-molecular-weight tetraalkyl ammonium salts which are more compatible with the matrix and give better results, as well as more suitable mediators for the thenoyltrifluoroacetone and valinomycin electrodes. Since Lutonal is compatible with many substances, it should be possible to find compositions as useful as $Ca(DEHP)_2$—decanol.

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REFERENCES

1 G. J. Moody, R. B. Oke and J. D. R. Thomas, Analyst (London), 95 (1970) 910.
2 F. A. Schultz, A. J. Petersen, C. A. Mask and R. P. Buck, Science, 162 (1968) 267.
3 J. W. Ross, Science, 156 (1967) 1378
4 K. Garbett and K. Torrance, IUPAC International Symposium on Selective Ion-Sensitive Electrodes. UWIST, Cardiff, April 1973, Paper No. 27; CERL, Laboratory Note No. RD/L/N 153/74, July 1974.
5 A. Craggs, L. Keil, G. J. Moody and J. D. R. Thomas, Talanta, 22 (1975) 907.
6 R. W. Cattrall, D. M. Drew and I. C. Hamilton, Anal. Chim. Acta, 76 (1975) 269.
7 O. F. Schäfer, Colloid Polym. Sci., 254 (1976) 628.
8 J. Kielland, J. Am. Chem. Soc., 59 (1937) 1675.
9 W. F. M. Vogel, Diplomarbeit, RWTH Aachen, 1976.
10 T. Higuchi, C. R. Illian and J. L. Tossounian, Anal. Chem., 42 (1970) 1674.
11 G. H. Griffiths, G. J. Moody and J. D. R. Thomas, Analyst (London), 97 (1972) 420.

Analytica Chimica Acta, 87 (1976) 499—503

Short Communication

ÉTALONNAGE D'UNE ÉLECTRODE SÉLECTIVE SENSIBLE AUX IONS CADMIUM(II) AU MOYEN DU SYSTÈME Cd(II)—ACIDE PYRIDINECARBOXYLIQUE-2

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Les électrodes indicatrices sélective sensibles à l'activité des ions cadmium libres en solution couvrent de larges domaines d'application [1—3]. L'utilisation d'une telle électrode spécifique nécessite un étalonnage préalable permettant d'obtenir une droite d'étalonnage de pente Nernstienne dans un large domaine de concentrations. On peut procéder par la mesure des potentiels d'électrode dans des solutions étalons préparées par une série de dilutions. Cependant les dilutions successives limitent rapidement la précision et il est difficile d'obtenir de bons résultats pour des pCd ($-\log [Cd^{2+}]$) inférieurs à 5. Nous proposons donc une méthode d'étalonnage dans laquelle la concentration du cadmium libre varie, de façon continue, en fonction du pH par complexation des ions Cd(II) à l'aide d'un coordinat convenablement choisi.

Une approche semblable a déjà été développée par Rûžička et Hansen [4] qui ont, notamment dans le cas du cadmium [5], utilisé une série de solutions tampons de pCd. Dans ce cas les agents complexants utilisés étaient les acides nitrilotriacétique et éthylènediaminotétraacétique, le pH des solutions étant fixé par l'utilisation des tampons acétate (pH 4,8) maléate (pH 6,5) et borate (pH 9). La difficulté de tels étalonnages réside dans le fait qu'il faut connaitre avec précision la valeur des constantes de stabilité ionique des complexes mis en jeu. L'utilisateur peut alors se référer à des ouvrages tels que celui de Ringbom [6], ou plus généralement aux tables des constantes établies par Sillen et Martell [7], mais il constatera souvent de larges divergences entre les valeurs déterminées par différents auteurs pour un même système complexe et le choix des constantes à utiliser devient alors délicat.

Nous envisageons, ici, le système Cd(II)—acide pyridinecarboxylique-2 (acide picolique; HA) qui nous a permis d'obtenir d'excellentes droites d'étalonnage dans le domaine $2,0 < pCd < 7,5$ soit $1,12 \cdot 10^3$ p.p.m. à $3,54 \cdot 10^{-3}$ p.p.m.

Partie expérimentale

L'électrode sélective utilisée est une électrode Tacussel type PCD1 [8] à élément actif interchangeable, récemment commercialisée. Les mesures de potentiels ont été effectuées à l'aide d'un millivoltmètre Tacussel type Isis 20 000, par rapport à une électrode de référence au calomel (jonction KCl saturé).

Les mesures de pH sont effectuées suivant le processus déjà décrit [9]; l'étalonnage de la chaine de mesure est vérifié quotidiennement à l'aide des solutions tampons de Bates [10]: biphtalate de potassium 0,05 M (pH 4,008) et borax 0,05 M (pH 9,196). La correspondance entre le pH lu et la concentration analytique des protons a été établie.

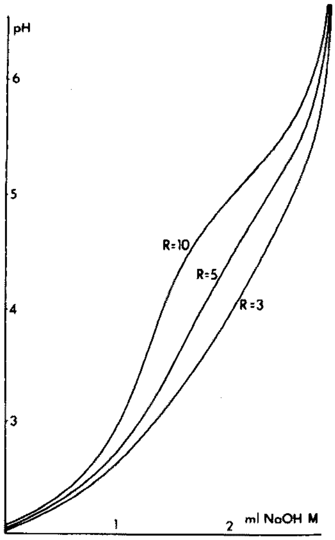
Toutes les mesures ont été faites, sous atmosphère d'azote; en cellules thermostatées Tacussel type RMO6, en milieu de force ionique 0,5 M maintenue constante par du nitrate de sodium (Merck p.a.) et à la température de 25 ± 0,1 °C.

Nous avons utilisé le nitrate de cadmium tétrahydraté (Merck p.a.). L'acide picolique a été synthétisé par la méthode de Black et al. [11] et purifié par trois recristallisations dans le benzène. Cependant cet acide est commercialisé dans un bon état de pureté et peut-être alors encore purifié facilement par sublimation.

Résultats

Le système Cd(II)—acide pyridinecarboxylique-2. L'examen de la littérature [7] montre des divergences sensibles concernant les constantes de dissociation protoniques de l'acide picolique et les constantes de stabilité ionique des complexes formés avec le cadmium. Nous avions étudié [12] ce système dans les mêmes conditions expérimentales ($NaNO_3$ 0,5 M; T = 25 °C) et après avoir déterminé les constantes de dissociation de l'acide picolique: $pK_1^H = 5{,}18$ et $pK_2^H = 0{,}87$ ($K_n^H = [H_{n-1}A] \cdot [H]/[HA]$), nous avions montré l'existence en solution des trois complexes successifs CdA^+, CdA_2 et CdA_3^- dont les constantes de stabilité globales $\beta_n = [CdA_n]/[Cd][A]^n$ ont été déterminées par des mesures précises de pH (méthode de Bjerrum) et de pCd grâce à une électrode à amalgame de cadmium (méthode de Leden). Les valeurs trouvées: $\log \beta_1 = 4{,}18$; $\log \beta_2 = 7{,}61$; $\log \beta_3 = 10{,}14$ sont celles utilisées dans ce travail.

Étalonnage de l'électrode. Nous avons neutralisé par la soude différentes solutions correspondant à trois rapports $R = C_A/C_M$ de réactifs engagés (C_A et C_M sont les concentrations totales de l'acide picolique et de l'ion métallique). Dans les trois cas on a: $NaNO_3 = 0{,}5$ M; $[HNO_3]_T = 10^{-2}$ M; $C_A = 1{,}872 \cdot 10^{-2}$ M et respectivement $C_M = 5{,}880 \cdot 10^{-3}$ M pour $R = 3$; $C_M = 3{,}920 \cdot 10^{-3}$ M pour $R = 5$; $C_M = 1{,}960 \cdot 10^{-3}$ M pour $R = 10$. Au cours de ces neutralisations, nous suivons simultanément les variations de pH (Fig. 1) et les variations du potentiel de l'électrode spécifique. Pour chaque valeur de pH, nous calculons alors la concentration en cadmium au sein des solutions à l'aide de notre programme général de calcul Acref 3AM [13] (disponible sur demande) qui permet de calculer la répartition de toutes les



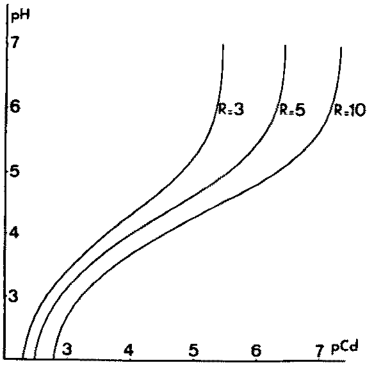


Fig. 1. Courbes de titrages pH = f(ml NaOH) des solutions de complexes métalliques.

Fig. 2. Courbes calculées pH = f(pCd).

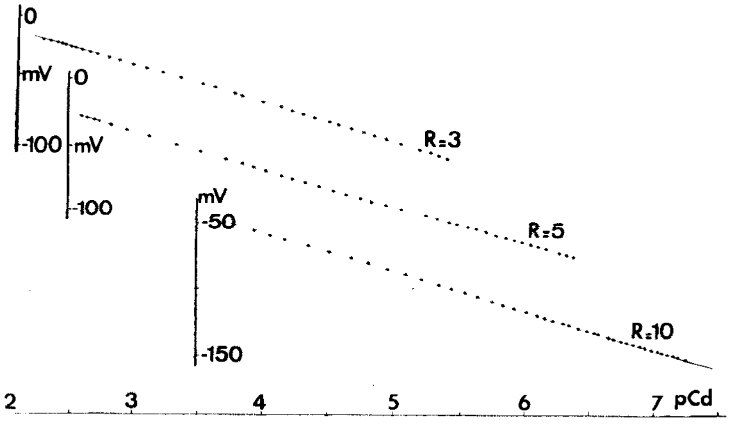


Fig. 3. Droites d'étalonnage de l'électrode spécifique (pour chaque rapport $R = C_A/C_M$, les ordonnées ont été décalées afin d'éviter une superposition des points expérimentaux correspondants).

espèces en solution en fonction du pH dans les cas les plus divers de formation de complexes métalliques simples binaires et mixtes ternaires et quaternaires.

En possession des courbes pH = f(pCd) (Fig. 2), on détermine les droites d'étalonnage *E* (potentiel de l'électrode sélective) = f(pCd) pour les trois cas étudiés. La Fig. 3 montre l'excellente linéarité obtenue pour différents domaines de pCd:

R = 3: 2,30 < pCd < 5,40 (37 points expérimentaux)
R = 5: 2,60 < pCd < 6,40 (41 points expérimentaux)
R = 10: 3,90 < pCd < 7,30 (42 points expérimentaux)

Les essais ont été répétés de façon systématique sur une durée d'environ un mois. Toutes les droites d'étalonnage obtenues présentent des pentes variant de 28,40 à 29,50 mV/pCd, restant donc dans tous les cas légèrement inférieures à la pente théorique de 29,58 mV/pCd (25 °C). D'autre part, les droites d'étalonnage se déplaçaient en fonction du temps vers les potentiels positifs avec une variation de l'ordre de 10 mV pendant un mois. Il importe donc dans le cas de déterminations précises de procéder à une étalonnage avant chaque utilisation de l'électrode.

Enfin, on remarque sur les courbes pH = f(pCd) (Fig. 2), que pour des pH voisins de 7, une variation importante de pH ne provoque qu'une faible variation de pCd. Par exemple, pour des pH compris entre 6,60—7,10, les variations correspondantes du pCd sont de 5,395 à 5,414 pour R = 3; de 6,372 à 6,398 pour R = 5 et de 7,256 à 7,286 pour R = 10. Nous observons une variation maximum du pCd de trois centièmes pour une variation de 0,5 unité de pH. On a donc de véritables zones tampons où la concentration des ions cadmium libres est sensiblement indépendante du pH. Ceci est particulièrement intéressant pour la mise en oeuvre de "solutions tampons de pCd" où le pH pourrait être fixé avec une faible précision alors que le pCd serait parfaitement défini.

Conclusions

Notre étude montre que la formation de complexes entre un ion métallique et un coordinat convenablement choisi, permet d'effectuer un étalonnage précis des électrodes indicatrices de l'activité de l'ion métallique libre en solution et ceci dans des domaines de faibles concentrations difficilement accessibles au moyen d'étalonnages par dilutions successives.

Ce concept a déjà été envisagé, notamment par Růžička et Hansen [5] et Perrin et Dempsey [14]. Cependant il faut bien entendu disposer de valeurs fiables, concernant les constantes de protonation du coordinat et les constantes de stabilité ionique des complexes métalliques formés, déterminées pour les mêmes conditions expérimentales que celles utilisées lors de l'étalonnage (température, nature de l'électrolyte support, force ionique). Růžička et Hansen [5], par exemple, ont utilisé pour le calcul du pCd les constantes tirées de l'ouvrage de Ringbom [6] (μ = 0,1, KNO_3). On remarque que d'autres espèces ont été signalées, par exemple, $CdA(OH)^{2-}$ dans le cas du NTA [15] et $CdHA^-$ dans le cas de l'EDTA [16].

Dans les conditions rappelées ci-dessus, notre programme de calcul, extrêmement général, permet de calculer les variations de la concentration des ions métalliques libres en fonction du pH et de tracer les droites d'étalonnage E = f(pM) qui dans le cas du cadmium(II) présentent une parfaite linéarité dans le domaine pCd 2,0—7,50 lorsque l'agent complexant est l'acide pyridinecarboxylique-2 [12]. D'autres coordinats peuvent être utilisés pour couvrir des domaines de pCd différents [5, 14, 17]. Les compositions et le pH de telles solutions pourraient être établies grâce à notre programme de calcul (comparable aux programmes Comics [18] ou Haltafall [19]. Il faut remarquer qu'il importe que le pH de ces solutions soit fixé par addition d'un réactif non complexant de préférence aux substances tampons (de pH) dont les composants sont souvent des agents complexants [14].

Enfin notre étude montre le bon fonctionnement de cette nouvelle électrode dans le domaine de pH étudié (2,50—7,20). Nous nous proposons d'examiner, ultérieurement et suivant le même processus, son comportement en milieu plus alcalin.

Nous remercions la Société Tacussel qui a mis à notre disposition une électrode spécifique PCD1 et Mademoiselle M. Autino pour sa collaboration technique.

BIBLIOGRAPHIE

1 J. Gardiner, Water Res., 8 (1974) 23.
2 G. J. M. Heijne et W. E. van der Linden, Talanta, 22 (1975) 923.
3 G. J. Moody et J. D. R. Thomas, in D. R. Williams (Ed.), An Introduction to Bioinorganic Chemistry, Thomas, Springfield, 1976.
4 E. H. Hansen, C. G. Lamm et J. Růžička, Anal. Chim. Acta, 59 (1972) 403.
5 J. Růžička et E. H. Hansen, Anal. Chim. Acta, 63 (1973) 115.
6 A. Ringbom, Complexation in Analytical Chemistry, Wiley-Interscience, New York, 1973.
7 L. G. Sillen et A. E. Martell, Stability Constants of Metal Ions Complexes, The Chemical Society, London, 1964, 1971.
8 J. P. Deloume, J. J. Fombon, F. Lancelot, J. M. Pâris, M. Roubin, J. Tacussel et J. C. Verdier, brevet en cours de dépôt.
9 M. Morin, M. R. Pâris et J. P. Scharff, Anal. Chim. Acta, 57 (1971) 123.
10 R. G. Bates, Determination of pH. Theory and Practice, Wiley-Interscience, New York, 1973.
11 G. Black, E. Depp et B. B. Corson, J. Org. Chem., 14 (1949) 14.
12 J. P. Scharff et M. R. Pâris, Bull. Soc. Chim. Fr., 8 (1968) 3184.
13 M. Cromer-Morin, R. P. Martin et J. P. Scharff, Compt. Rend., 277 (1974) 1339.
14 D. D. Perrin et B. Dempsey, Buffers for pH and Metal Ion Control, Chapman and Hall, London, 1974, pp. 94—108.
15 G. Schwarzenbach et W. Biedermann, Helv. Chim. Acta, 31 (1948) 331.
16 G. Anderegg, Helv. Chim. Acta, 47 (1964) 1801.
17 H. U. Wolf, Experimentia, 29 (1973) 241.
18 D. D. Perrin et I. G. Sayce, Talanta, 14 (1967) 833.
19 N. Ingri, W. Kakalowicz, L. G. Sillen et B. Warnquist, Talanta, 14 (1967) 1261.

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Short Communication

N-BROMOSUCCINIMIDE AS A REDOX TITRANT IN THERMOMETRIC TITRIMETRY

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N-Bromosuccinimide as a reagent for the determination of organic compounds, has been extensively reviewed by Mathur and Narang [1], whilst Berka et al. [2] have briefly reviewed its use for the determination of some inorganic and organic compounds. Barakat et al. [3] were among the first to report the use of *N*-bromosuccinimide as a volumetric reagent for the direct titration of ascorbic acid in pharmaceutical products, edible fruits and some biological fluids; they used starch as the indicator. Evered [4] reported the titration of ascorbic acid in highly coloured solutions with an extraction end-point.

Many of the problems associated with the use of *N*-bromosuccinimide in industrial analysis, arise from the presence of coloured and/or insoluble materials in the sample provided. Thus visual methods for detection of the equivalence point may be subject to error; measurements of potentials often fail because of the surface-active materials present and the relatively low conductivity of many of the sample solutions. Thermometric methods have been used successfully in such solutions on many occasions, including direct assay of foodstuff constituents [5]. The usefulness of *N*-bromosuccinimide results from its high oxidation potential, from its selectivity under appropriate conditions, and from its applicability in various types of reactions such as oxidation, substitution and addition. It was decided to restrict the present investigation to its use as an oxidant. For a compound to be accepted as a titrant in thermometric analysis, it must meet only the requirements of classical titrimetry, but must also have a relatively high solubility (since concentrated titrants are generally used), or the overall enthalpy change of the reaction must be high, so that an acceptable sensitivity may be obtained when dilute solutions are assayed.

Preliminary investigations indicated that the molar enthalpy changes for the reactions between *N*-bromosuccinimide and several of the reductants studied are about 250 kJ mol^{-1}. For sample solutions of about 0.01 M and at least 0.1 M titrant solutions, a suitable sensitivity can be obtained if ΔH

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exceeds 16 kJ mol^{-1}. Thus, although *N*-bromosuccinimide is not very soluble (a saturated solution is approximately 0.08 M), a suitable precision can be obtained for 10^{-3} M analyte solutions.

Experimental

Apparatus and reagents. The circuit for the basic bridge system used, and details of the titration assembly have been reported previously [6]. The compounds used were analytical-reagent grade and were assayed by appropriate standard methods [7].

Since *N*-bromosuccinimide dissolves only slowly at room temperature, it should be dissolved in hot (80 °C) water. Aqueous solutions are not very stable; after preparation and standing in sunlight for a few hours, the bromine liberated can be observed. However, the solutions are stable for 3 days if they are stored at about 4 °C and protected from sunlight. Although *N*-bromosuccinimide can be obtained in a relatively pure form, its solutions should be standardized before use, against standard arsenic(III) solution in 2 M HCl, the equivalence point being indicated thermometrically.

General procedure. A known amount of the sample is transferred to the reaction—titration vessel, in the required reaction medium, and the volume adjusted to 10 ml. Then the solution is titrated, thermometrically, with standard *N*-bromosuccinimide solution (0.0725 M). In all cases, the sensitivity and the recorder chart speed were set to 2mV for f.s.d and 30 mm min^{-1}, respectively. The titrant was delivered at a rate of 0.259 ml min^{-1} (determined gravimetrically). Thus 1 ml of solution is equivalent to 116 mm of chart distance, or 1 μmol of *N*-bromosuccinimide corresponds to a distance of 1.6 mm.

Results and discussion

Some typical results are given in Table 1. The enthalpograms are of four types.

Type 1 Enthalpogram. This shows the normal type of exothermic single-stage reaction with acceptable kinetics. Any compound which gives this type of curve can be determined without extrapolation being needed to locate the equivalence point. For the 5—50-μmol range (in 10 ml of solution), the precision is generally within 1—2 %.

Type 2 Enthalpogram. The enthalpogram for sodium iodide shows two equivalence points; the first is well defined and corresponds to the formation of iodine; the second is less well defined, must be located by extrapolation, and corresponds to the formation of iodine monochloride or monobromide (since the titration medium is 2 M HCl, either or both may be formed).

Type 3 Enthalpogram. Only ammonium thiocyanate shows this type of enthalpogram; the first equivalence point corresponds to the oxidation of thiocyanate to sulphate and succinimide. The second heat rise is caused by the slow onset of the reaction of bromine with ammonium ion to form nitrogen and possibly some nitrogen oxides [8].

TABLE 1

Results for various samples

Sample (medium)	Stoichiometry Reagent/Analyte	Taken (μmol)	Found[a] (μmol)	Recovery (%)	Type of Enthalpogram
$NaAsO_2$		10	9.7	97	
(0.1—2 M HCl)	1 : 1	20	19.4	97	1
or (0.01—0.05 M NaOH)		40	38.8	97	
		5	4.9	98	
NH_4SCN	4 : 1	10	9.8	98	3
($NaHCO_3$pH7—8)		20	19.5	97.5	
KSCN		4	4.05	101	1
($NaHCO_3$pH7—8)	4 : 1	8	8.1	101	
SbO. $C_4H_6O_6$	1 : 3	10	10	100	
(1—3 M HCl)		20	20	100	1
		25	25.2	101	
		10	9.9	99	
NaI	1 : 2	20	20	100	2
(2 M HCl)		40	40	100	
		20	19.7	98.5	
Hydroquinone	1 : 1	40	39.4	98.5	1
(0.1—1 M HCl)		50	49.1	98	
Thiourea	4 : 1	5	49.5	99	
($NaHCO_3$pH7—8)		10	98.6	99	1
		15	149	99	
Ascorbic acid	1 : 1	10	98.7	99	
(0.1—1.0 M HCl)		20	197	98	1
		25	247	99	
$N_2H_5HSO_4$[b]	2 : 1	10	10.1	101	
		20	20.3	101	1
		30	30.3	101	
$N_2H_4 \cdot H_2O$[b]	2 : 1	28.5	28.7	101	1
		57.0	57.4	101	
Monomethylhydrazine[b]	2 : 1	26.3	26.7	102	1
		52.6	53.1	101	
UDMH[b]	2 : 1	14.6	14.9	102	
		29.2	29.6	101	4
		43.8	44.5	102	

TABLE 1 (continued)

Sample (medium)	Stoichiometry Reagent/Analyte	Taken (μmol)	Found[a] (μmol)	Recovery (%)	Type of Enthalpogram
Phenylhydrazine hydrochloride[b]	2 : 1	10	10	100	1
		20	20	100	
		30	29.8	99	
4-Nitrophenylhydrazine[b]	2 : 1	5	49	98	1
		10	98	98	
		15	147	98	
2,4-Dinitrophenylhydrazine[b]	2 : 1	5	49	98	1
		10	97	97	
		20	194	97	
Semicarbazide[b]	2 : 1	10	10	100	1
		20	20	100	
		30	29.8	99	
1-Phenylsemicarbazide[b]	1 : 1	10	10	100	1
		20	20	100	
		30	30.3	101	
Isonicotinic acid hydrazine[b]	2 : 1	5	5	100	1
		10	10	100	
		20	20.3	102	

[a] Average of at least 3 results.
[b] In 1—2 M HCl.

Type 4 Enthalpogram. This type is shown only by unsymmetrical dimethylhydrazine (UDMH). The first equivalence point corresponds to a stoichiometry of 2 NBS: 1 UDMH; the second, more exothermic reaction probably involves bromination.

The method for isonicotinic acid hydrazide was applied to anti-tubercular preparations in tablet form; the results indicated that the excipients have no effect on the reaction.

These results show that *N*-bromosuccinimide is a useful titrant in thermometric analysis, when used as an oxidant. Studies of its other functions are in progress.

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REFERENCES

1 N. K. Mathur and C. K. Narang, Determination of Organic Compounds with *N*-Bromosuccinimide and Allied Reagents, Academic Press, London, 1975.
2 A. Berka, J. Vulterin and J. Zyka, Newer Redox Titrants, Pergamon Press, London, 1965, pp. 52—54.
3 M. Z. Barakat, M. F. Wahab and M. M. Sadr, Anal. Chem., 27 (1955) 536.
4 D. F. Evered, Analyst (London), 85 (1960) 515.
5 L. S. Bark, D. Griffin and P. Prachuabpaibul, Analyst (London), 101 (1976) 306.
6 L. S. Bark and P. Bate, Analyst (London), 96 (1971) 881.
7 Analar Standards for Laboratory Chemicals, B.D.H. Ltd., Poole, UK.
8 I. M. Kolthoff and R. Belcher, Volumetric Analysis III, Interscience, New York, 1957, p. 582.

Analytica Chimica Acta, 87 (1976) 511—514

Short Communication

TITRATION OF ARSENIC(III) WITH CERIUM(IV) SULPHATE IN AQUEOUS SULPHURIC ACID AND ACETIC ACID MEDIA

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Willard and Young [1] proposed the potentiometric titration of arsenic(III) in about 2.26—3.4 M hydrochloric acid medium with 2.5—20 ml of 0.005 M iodine monochloride as catalyst per 100 ml of the titration mixture; the error was 0.3 %. On investigating the effect of hydrochloric acid concentration, Swift and Gregory [2] found that for accurate titrations the concentration of hydrochloric acid at the end-point should be at least 4 M, even when extractive end-points were used. The hydrochloric acid effect noted by Swift and Gregory has been confirmed here, although it is unexpected on theoretical grounds in view of the increase in the formal potential of the arsenic(V)—arsenic(III) couple with increasing hydrochloric acid concentration. This formal potential (with 0.005 M arsenic solutions) increases from 0.253 V at pH 7 to 0.526 V at pH 3, 0.604 V in 2 M HCl, 0.646 V in 4 M HCl, and 0.808 V in 8 M HCl [3].

The odd behaviour mentioned above must be due to the difficulty of potential equilibration at the lower hydrochloric acid concentration and not to kinetic factors, as there is enough catalyst present. The titration of arsenic(III) with cerium(IV) sulphate in other acidic media was therefore studied; sulphuric acid and acetic acid media were selected for the purpose.

Experimental

Reagents. For the arsenic(III) solution (0.025 M), AnalaR arsenic trioxide was dissolved in 0.6 M sodium hydroxide, and the solution was made ca. 0.15 M in sulphuric acid and diluted to volume. It was standardized by two different methods [4, 5]. A 0.05 M cerium(VI) sulphate solution in 0.5 M sulphuric acid was prepared and standardized [6, 7]. For the catalyst mixture, 20.8 ml of 0.1 M potassium iodide and 4.16 ml of 0.1 M potassium iodate were mixed and diluted to 250 ml. Iodine monochloride (0.005 M) and ferroin (0.01 M) were prepared as prescribed by Kolthoff and Belcher [8]. Merck's Pro Analysi acetic acid was used; other brands of acetic acid, although of analytical-reagent grade, contained traces of reducing impurities which reacted with cerium(IV) sulphate, in presence of ferroin indicator.

For example, 5 ml of one brand of acetic acid consumed 0.04 ml of 0.05 M cerium(IV) sulphate. All other chemicals used were analytical grade.

Potentiometric titration assembly. A Junior potentiometer (Pye) was used with a galvanometer, a saturated calomel reference electrode and a bright platinum rod (ca. 0.2 mm diameter) indicator electrode. The salt bridge was an inverted "U" tube with porous plate ends filled with a saturated solution of potassium chloride.

Titrations in aqueous sulphuric acid medium. Accurate titrations are possible in 0.5—1.5 M sulphuric acid, with 0.5—1.0 ml of iodate—iodide mixture as catalyst. The potentials stabilize within 1 min in the early stages, and within 3 min at 0.2 ml before the end-point. In 0.5 M sulphuric acid medium the end-point potential jump is ca. 180 mV for 0.04 ml of 0.05 M cerium(IV) sulphate, and 250 mV in 1.5 M sulphuric acid. It is interesting that accurate potentiometric titrations are possible in 0.5 M sulphuric acid, whereas a minimum of 4.4 M hydrochloric acid is required.

Accurate visual titrations are possible in 0.5—2.0 M sulphuric acid medium with 0.3—0.5 ml of the iodate—iodide catalyst for 50 ml of the titrand and 0.05 ml of 0.01 M ferroin as indicator. During the titration, the deep brown colour of iodine comes and goes; with magnetic stirring rapid titration is possible until near the end-point, and then 10 s should be allowed between drops. The end-point is indicated by a colour change from brown to the light yellow of iodine, and is quite different from the usual ferroin end-point. The brown colour is emphasized when more catalyst is used, and is due to a ferroin—triiodide complex. The appearance of the brown colour indicates the approach of the end-point. The end-point colour is stable for over 2 h. Typical results are given in Table 1. This procedure constitutes a great improvement over the procedure of Willard and Young which is burdened with many problems [5, 8].

Titrations in aqueous acetic acid medium. As arsenic(III) is slowly oxidized at low hydrogen ion concentration by atmospheric oxygen, possible aerial oxidation of arsenic(III) in aqueous acetic acid (10—30 %) was examined, but there was no effect for at least 10 h. Potentiometric titrations were done in 20 % and 30 % aqueous acetic acid; the sulphuric acid concentration was ca. 0.1—0.15 M and 0.2—1.0 ml of the iodate—iodide mixture was used as catalyst. In 30 % acetic acid, the potentials stabilized within 1 min in the early stages and within 2 min near the end-point. Stabilization was slower in 20 % acetic acid. The potential jump at the end-point in 30 % acetic acid was about 170 mV for 0.04 ml of 0.05 M cerium(IV) solution. The formal potential of the As(V)/As(III) couple decreased from 0.710 V to 0.640 V as the amount of catalyst added increased from 0.2 to 1.0 ml, but was unaffected by a decrease in the acetic acid concentration to 20 %.

Visual titrations of arsenic(III) were done in 10, 20 and 30 % acetic acid media, in presence of 0.1—0.15 M sulphuric or 0.2—0.3 M hydrochloric acid. Here, the ferroin colour persists throughout the titration, although its

TABLE 1

Titration of arsenic(III) with cerium(IV) sulphate in dilute sulphuric acid medium with ferroin as indicator

As taken (meq)	As found (meq)		
	0.5 M H_2SO_4	1.0 M H_2SO_4	2.0 M H_2SO_4
0.2000	0.1995	0.2002	0.1994
0.2500	0.2497	—	0.2500
0.3000	0.2998	—	—
0.3250	—	0.3244	0.3243
0.3500	0.3510	—	0.3508
0.4250	—	0.4260	0.4256
0.4500	0.4509	—	0.4509
0.5000	—	0.5000	0.5008

intensity is reduced when 0.5—1.0 ml of 0.005 M iodine monochloride is used in 50 ml of titrand. At the end-point the colour changes sharply from orange-red to pale blue, and does not return even after 10 min. When iodine monochloride is used, results are erratic if the mineral acid is omitted, but this does not happen with the iodide—iodate mixture. With this catalyst mixture (0.3—0.5 ml) a transient brown colour appears, and titration must be done slowly near the end-point; the colour change is from brown to yellow. Typical results are given in Table 2.

Varying the concentration of sulphuric acid in the limits 0.15—0.5 M did not affect the titration in 10, 20 and 30 % acetic acid, when iodate—iodide was used as catalyst. With iodine monochloride as catalyst, variation of the hydrochloric acid concentration from 0.3 to 1.0 M had no effect.

pH *of test solutions.* The pH values of solutions containing acetic acid and dilute sulphuric acid were carefully checked. In 20—30 % acetic acid medium, where the electrometric titrations were conducted with 0.2 ml of the catalyst mixture, the pH was 1—0.8. The formal potential of the As(V)/

TABLE 2

Titration of arsenic(III) with cerium(IV) sulphate in aqueous acetic acid with ferroin as indicator (All results are given in meq.)

Iodate-iodide mixture				Iodine monochloride		
10 % HAc		30 % HAc			10 % HAc	30 % HAc
As taken	Found	As taken	Found	As taken	Found	Found
0.2500	0.2500	0.2770	0.2770	0.1934	0.1938	0.1934
0.3000	0.2999	0.2830	0.2828	0.2420	0.2420	0.2420
0.3500	0.3497	0.3190	0.3187	0.2903	0.2900	0.2910
0.4000	0.3998	0.3790	0.3788	0.3395	0.3395	0.3390
0.4500	0.4499	0.4420	0.4418	0.4355	0.4365	0.4370

As(III) couple should therefore be 0.562—0.565 V, but the values observed were about 0.71 V. This increase indicates preferential complexation of the arsenic(III) compared to the arsenic(V); clearly the complexation of arsenic(III) is almost complete even in 20 % acetic acid. This increase in the formal potential obviously contributes to the resistance of arsenic(III) to aerial oxidation.

Discussion

Early work [1, 2] indicated that high acidity is essential for successful titration of arsenic(III) with cerium(IV) sulphate. However, the present work has shown that arsenic(III) can be titrated successfully even in acetic acid medium. Moreover, visual titrations in acetic acid medium with ferroin indicator are more facile than in a medium containing a high concentration of hydrochloric acid [2]. Willard and Young [9] later reported that the chloride concentration is more critical than the hydrogen ion concentration. However, the presence of chloride was found to reduce the speed of reduction of the oxidized ferroin by arsenic(III) in acetic acid medium, in the present study.

During visual titrations of arsenic(III) in aqueous sulphuric acid or acetic acid media with the iodate—iodide catalyst, a transient brown colour was observed; this brown colour disappeared slowly near the end-point, and was clearly different from the orange-red of ferroin. Tests with different amounts of 10^{-2} M solutions of ferroin, iodine and iodide showed that the brown colour is due to the complex $Fe(Phen)_3^{2+}—2I_3^-$. The brown colour did not appear until a sufficient excess of both iodine and iodide was present. Addition of cerium(IV) destroyed the brown colour, thus proving that ferroin is an essential component. Addition of arsenic(III) also destroyed the brown complex, but this reaction is slow; when arsenic(III) equivalent to the iodine present was added, there was only partial reduction of the brown colour even in 2.5 min. However, when all the iodine had reacted with arsenic(III), the brown colour disappeared. At this stage, addition of a little cerium(IV) restored the brown colour, because of the liberation of iodine by interaction of iodide with cerium(IV) and reaction of this iodine with iodide and ferroin. The oxidation of iodide in the complex by cerium(IV) is faster than the reaction of arsenic(III) with iodine or the catalysed oxidation of arsenic(III) by cerium(IV).

REFERENCES

1 H. H. Willard and P. Young, J. Am. Chem. Soc., 50 (1928) 1372.
2 F. H. Swift and C. H. Gregory, J. Am. Chem. Soc., 52 (1930) 901.
3 W. Petzold, Die Cerimetrie, Verlag Chemie, Weinheim/Bergstr., 1955, p. 142.
4 H. A. Bright, Ind. Eng. Chem., Anal. Ed., 9 (1937) 577.
5 M. Gandikota and G. Gopala Rao, Anal. Chim. Acta, 65 (1973) 231.
6 H, H. Willard and P. Young, J. Am. Chem. Soc., 50 (1928) 1322.
7 V. Panduranga Rao and G. Gopala Rao, Talanta, 2 (1959) 370.
8 I. M. Kolthoff and R. Belcher, Volumetric Analysis, Vol. III, Interscience, New York, 1957, p. 44, 127.
9 H. H. Willard and P. Young, J. Am. Chem. Soc., 55 (1933) 3260.

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Short Communication

AMPEROMETRIC COMPLEX-FORMATION TITRATIONS OF TRACES OF CATIONS

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(Received 4th June, 1976)

The titration of very dilute solutions of metal ions which form very stable complexes with ligands such as EDTA can be reasonably selective when carried out at low pH. When the reaction between the metal ion and the ligand is slow, a back-titration procedure is the obvious solution. Examples of such back-titrations have been described [1, 2] for indium(III) and chromium(III), the end-point being indicated by the anodic wave of the free ligand at a rotating mercury electrode. The present communication discusses titrations of gallium and zirconium, as well as the use of a microcell.

Back-titration of traces of gallium

Gallium(III) reacts slowly with EDTA in very dilute solutions. The stability constant for the gallium(III)—EDTA complex is $10^{20.5}$, but a GaHL complex is formed in acidic solutions ($\log K^{H}_{GaHL} = 1.7$), so that the conditional stability constant, $\log K'$, lies between 7 and 8 at pH 2. This means that the limit of determination for gallium(III) should be slightly above 10^{-6} M at pH.2. Bismuth(III) is the most appropriate metal ion for the back-titration. Any metal ion forming a complex with EDTA under the experimental conditions interferes, as the indicator electrode does not register the displacement of metal ions forming complexes weaker than that with bismuth(III) [1].

Procedure. The experimental set up was the same as described previously. Put a sample containing about 5 nmol of gallium(III) (0.35 μg) in 5 ml of perchloric acid of pH 2 in the titration cell, and add 10 nmol of EDTA. Titrate the excess of EDTA with $5 \cdot 10^{-4}$ M bismuth(III); the potential of the indicator electrode should be + 0.35 V vs. SCE. Locate the end-point by intersecting the two straight branches of the titration curve.

Results. The determination of 10^{-6} M gallium(III) (0.35 μg) showed a standard deviation of 3 % (n = 10). The effects of some other substances on the determination were examined; iron(III) and, of course, bismuth(III) interfered. The interference of aluminium(III) could be overcome by masking with fluoride. Some results are given in Table 1.

TABLE 1

Determination of gallium(III) in the presence of other ions (0.350 μg Ga(III) taken in each case)

Diverse ion (X)	Molar ratio X:Ga	Ga found (μg)	Error (%)	s_r (%) (no. of detns.)
As(III)	1000	0.364	+ 4	2 (9)
Zn(II)	100	0.340	− 3	2 (8)
Al(III)	10	0.380	+ 9	4 (8)
Al(III)[a]	100	0.339	− 3	4 (5)
Pb(II)	5	0.350	—	6 (7)
Chloride	10	0.346	− 1	4 (6)

[a] With 10^{-3} M fluoride added.

Back-titration of some other metal ions

The possibility of similar determinations for thallium(III) and zirconium(IV) was investigated. In the case of thallium, difficulties arose in keeping thallium in the tervalent state, and no useful results could be produced. Greater success was achieved with zirconium(IV). The stability constant of the zirconium complex with EDTA is about 10^{27}, so that selective titration should be possible in quite acidic solutions, which are also necessary to avoid the formation of hydroxo complexes. Complex formation in dilute solutions is slow, so that heating of zirconium(IV) with EDTA is necessary to ensure complete complex formation. Determinations of $5 \cdot 10^{-6}$ M zirconium(IV) are possible in perchloric acid media of pH 1.

Procedure. Add to 5 ml of $5 \cdot 10^{-6}$ M zirconium(IV) (pH 1, perchloric acid), 50 nmol of EDTA. Heat on a boiling water bath for 10 min. Cool and titrate with $5 \cdot 10^{-3}$ M bismuth(III), as described above.

Results. The determination of $5 \cdot 10^{-6}$ M zirconium(IV) (about 2.5 μg in 5 ml) showed a standard deviation of 5 % (n = 13). The influence of some other ions was investigated. Iron(III) and bismuth(III) interfere but these elements can be separated from zirconium(IV) by electrolysis at a mercury pool cathode. This also applies to copper(II) which, however, does not interfere when present in a 10-fold amount with respect to zirconium. A 500-fold amount of aluminium and a 500-fold amount of zinc do not interfere. In all cases the standard deviation is between 3 % and 5 %. No systematic deviations were observed.

Determinations in a microcell

The use of a rotating mercury electrode in a microcell was studied briefly. As the indicating reaction at the electrode is the anodic dissolution of mercury as its chelate with the ligand, some error is always introduced. As the determinations require only a short time, this error is generally negligible when a 10-ml cell, as described previously, is used. When smaller cell volumes are associated with the same electrode surface area, the error caused by the indicating reaction at the electrode increases as the cell volume decreases. Titrations in a 0.05-ml cell failed, mainly for this reason, but titrations in a 0.5-ml cell proved to be possible.

The very simple cell used did not differ much from the 10-ml cell used previously. The 0.5-ml titration cell, with a G4 glass sinter at the bottom, was fitted into the reference solution contained in an H-cell. The area of the electrode was 2.7 mm^2 instead of the 13.5 mm^2 in earlier experiments.

Some titrations of 10^{-6} M copper(II) with 10^{-4} M Trien in a solution which was 10^{-2} M in KNO_3 and 10^{-2} M in Tris buffer pH 9 were carried out. After every 1-μl increment of the titrant, a waiting time of 20 s was observed before the current was read, so that the time required for a titration was less than 5 min. The standard deviation on 9 determinations was 4 % and no significant systematic error was observed. Thus the determination of 0.5 nmol of copper(II) (30 ng) was possible in this simple manner.

REFERENCES

1 Th. J. M. Pouw, G. den Boef, U. Hannema, J. M. van der Meer and S. Q. J. Zonneveld, Anal. Chim. Acta, 68 (1974) 137.
2 G. den Boef and R. Oostervink, Anal. Chim. Acta, 72 (1974) 434.

Analytica Chimica Acta, 87 (1976) 519—20

Book Reviews

F. Matsumara, *Toxicology of Insecticides*, Plenum Press, New York, 1975, xvii + 503 pp., price $33.

This book, intended for students and the general scientific community rather than those already expert in the field, was written by Professor Matsumara whilst on sabbatical leave at the University of Hawaii. Matsumara certainly spent little time sunbathing on the beach. Matsumara prefers single-authored books "for a better basic understanding of a scientific field" and relies on the good, old-fashioned "do it the hard way" type of personal literature survey as a result of previous disappointments with computerised methods; his aim to produce a self-contained volume to enable the reader to develop rapidly a basic understanding of this complex field has been achieved with great success. This is one of the most interesting, stimulating and useful books seen for quite some time; it is beautifully produced, and the price is very reasonable by today's standards.

The chapters of this book deal with General Principles of Insecticide Toxicology, Classification of Insecticides, Mode of Action of Insecticides, Metabolism of Insecticides by Animals and Plants, Entry of Insecticides into Animal Systems, Dynamics of Insecticide Movement in the Animal Body, Movement of Insecticides in the Environment, Environmental Alteration of Insecticide Residues, Effect of Pesticides on Wildlife, Hazards to Man and Domestic Animals. There are Author and Subject Indexes, a comprehensive Table of Contents, and many tables that present a great deal of factual information.

Analytical methods for insecticides are briefly considered in terms of sampling, extraction, and clean-up; separation and detection (mostly chromatographic); chemical reactions; spectroscopic methods; biological and biochemical assay. This does not purport to be an analytical text — but the general background information it provides and its inter-disciplinary approach will be of great value to analytical chemists and all environmentalists.

D. M. W. Anderson

Colloque International sur l'Analyse par Activation de très faibles quantités d'Éléments, Akademiai Kiado, Budapest, 1975, viii + 888 pp., price £36.10.

This very substantial book contains the Proceedings of the International Conference which took place in Saclay in October 1972. There are some 80 contributions to most aspects of the field of activation analysis.

As one would expect, the Proceedings represents an interesting and valuable collection of work. However, it is difficult to understand why the Publishers should have bothered to offer the book for general sale at the particular time they did. Those interested in activation analysis, but who were unable to be in Saclay, would almost certainly have made a point of reading the entire proceedings as soon as they were originally published during 1973 and 1974 in the Journal of Radioanalytical Chemistry (Volumes 17—19). Of course, there are advantages in possessing one's own copy; but many individuals will balance any inclination to purchase a copy of the same Proceedings, now published in this form, against the rather high asking price.

At such a price, one could expect at least consecutive pagination. The pagination system, directly inherited from three volumes of J. Radioanal. Chem., involves pages 9—186 occurring thrice and many similar examples could be quoted. This may very well cause confusion when a paper in the Proceedings is quoted and it is my opinion that if there are sound commercial reasons for re-publishing them, some effort should have been made to alter the presentation.

L. Graham

ANALYTICA CHIMICA ACTA, VOL. 87 (1976)

AUTHOR INDEX

ANALYTICA CHIMICA ACTA, VOL. 87 (1976)

SUBJECT INDEX

Detectors in Gas Chromatography

by JIŘÍ ŠEVČÍK, *Department of Analytical Chemistry, Charles University, Prague.*

JOURNAL OF CHROMATOGRAPHY LIBRARY, Vol. 4

1976. 192 pages. US $23.95/Dfl. 60.00. ISBN 0-444-99857-8

This publication is devoted to the function and optimal working conditions of gas chromatographic detectors. The first systematic treatment of gas chromatographic detection techniques, it devotes special attention to so-called specific detectors and working conditions which strongly influence results (e.g. gas flow, effect of additives in gases, working temperature, detector form and dimensions). Anomalous detector responses are explained and the form and size of a response under various working conditions are indicated. The problems presented are illustrated by experimental data which are summarized in numerous tables and figures. The book should be of interest to all who use gas chromatography in research and who would like to explore the possibilities and working conditions of different detector systems.

CONTENTS: 1. **Introduction.** Concentration distribution of the eluted substance at the column outlet. Detector signal. Effect of the measuring device on the signal changes. Sample injection. Parameters characterizing detectors. **2. The Thermal Conductivity Detector (TCD).** Detection mechanism. Signal of the TCD. Effect of experimental parameters on the magnitude and shape of the TCD. Applications of the TCD. **3. Ionization Detectors.** Physical principles of the detection. Ionization energy sources. Reactions in the ionization detector. **4. The Electron Capture Detector(ECD).** Detection mechanism. ECD signal. Experimental conditions affecting the ECD signal. Applications of the ECD. **5. The Flame Ionization Detector (FID).** Detection mechanism. FID signal. Experimental conditions affecting the magnitude and character of the FID signal. FID applications. **6. The Thermionic Detector Using an Alkali Metal Salt (TIDA).** Detection mechanism. TIDA signal. Effect of the experimental conditions on the magnitude and character of the TIDA signal. TIDA applications. **7. The Photoionization Detector (PID).** Detection mechanism. PID signal. Effect of the experimental conditions on the PID signal. PID applications. **8. The Helium Detector (HeD).** Detection mechanism. HeD signal. Effect of experimental conditions on the HeD signal. HeD applications. **9. The Flame Photometric Detector (FPD).** Detection mechanism. FPD signal. Effect of experimental conditions on the magnitude of the FPD signal. Use of the flame photometric detector. **10. The Coulometric Detector (CD).** Detection mechanism. CD signal. Effect of experimental conditions on the magnitude of the CD signal. Applications of the CD **11. The Electrolytic Conductance Detector (ElCD).** Detection mechanism. ElCD signal. Construction of the ElCD. Applications of the ElCD. **Subject index.**

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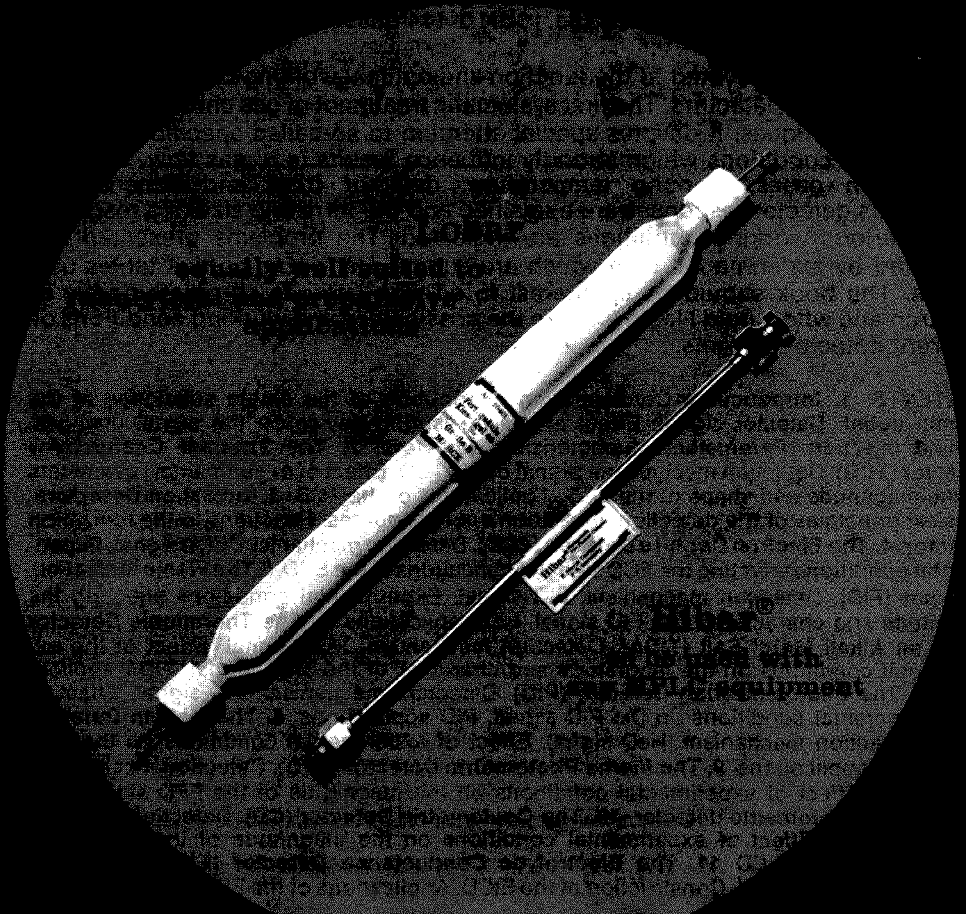
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(continued from page 4 of cover)

Short Communications

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CONTENTS

(continued on inside page of the cover)