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Vol. **59**, No. **3**	May 1972	**(completing Vol. 59)**
Vol. **60**, No. **1**	June 1972	
Vol. **60**, No. **2**	July 1972	**(completing Vol. 60)**
Vol. **61**, No. **1**	August 1972	
Vol. **61**, No. **2**	September 1972	
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Rutherford - Recollections of the Cambridge Days

by MARK OLIPHANT, *Government House, Adelaide;*
formerly Research School of Sciences,
The Australian National University, Canberra.

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Ernest Rutherford attended Canterbury College, the University of New Zealand, and subsequently entered Trinity College, Cambridge, as a research student at the Cavendish Laboratory. When the Macdonald Chair of Physics at McGill University, Montreal, became vacant in 1898, he took up the post. There was ample opportunity for research at McGill and his work on radioactive bodies, particularly on the emission of alpha rays, was continued in the Macdonald Laboratory.

Rutherford returned to England in 1907 to become Langworthy Professor of Physics at the University of Manchester. It was during this period that his investigations into the scattering of alpha rays and the nature of the inner structure of the atom resulted in his greatest contribution to physics, his concept of the "nucleus". This eventually led to the theory of atomic structure which with later improvements, remains valid to this day. In 1908, when Rutherford was awarded the Nobel Prize for Chemistry, he reached the highest peak of eminence which any man of science could hope to attain. As the greatest physicist in the world, it was surprising that he should receive the Prize for Chemistry, but in fact the work that he had done was concerned almost as much with chemistry as with physics.

In 1919 he accepted an invitation to assume the position of Cavendish Professor of Physics at Cambridge. An inspiring leader of the Cavendish Laboratory, Rutherford steered numerous future Nobel Prize winners towards their great achievements and it has been pointed out by C. D. Ellis, his co-author in 1919 and 1930, that "the majority of the experiments at the Cavendish were really started by Rutherford's direct or indirect suggestions". He remained active and working until his death in 1937.

The author, one of the very few who worked closely with Lord Rutherford, and who knew him and Lady Rutherford personally, records here his recollections of Rutherford at home, on holiday and in the laboratory, together with such memories of this great man of science as he has been able to obtain from contemporaries, colleagues and students. The Foreword, written by Sir James Chadwick, gives additional insight into the character and achievements of Lord Rutherford.

CONTENTS: Introduction. 1. The Cavendish Laboratory. 2. Counting, money, and mass spectroscopy. 3. Radio, junk, tea, visitors. 4. Injustice, history. 5. Chadwick and the neutron. 6. Cockcroft and Walton. 7. The crocodile. 8. Working with Rutherford. 9. Home, holidays, politics. 10. Rutherford and nuclear energy. 11. Directing research, D.S.I.R., science and people. 12. The end.

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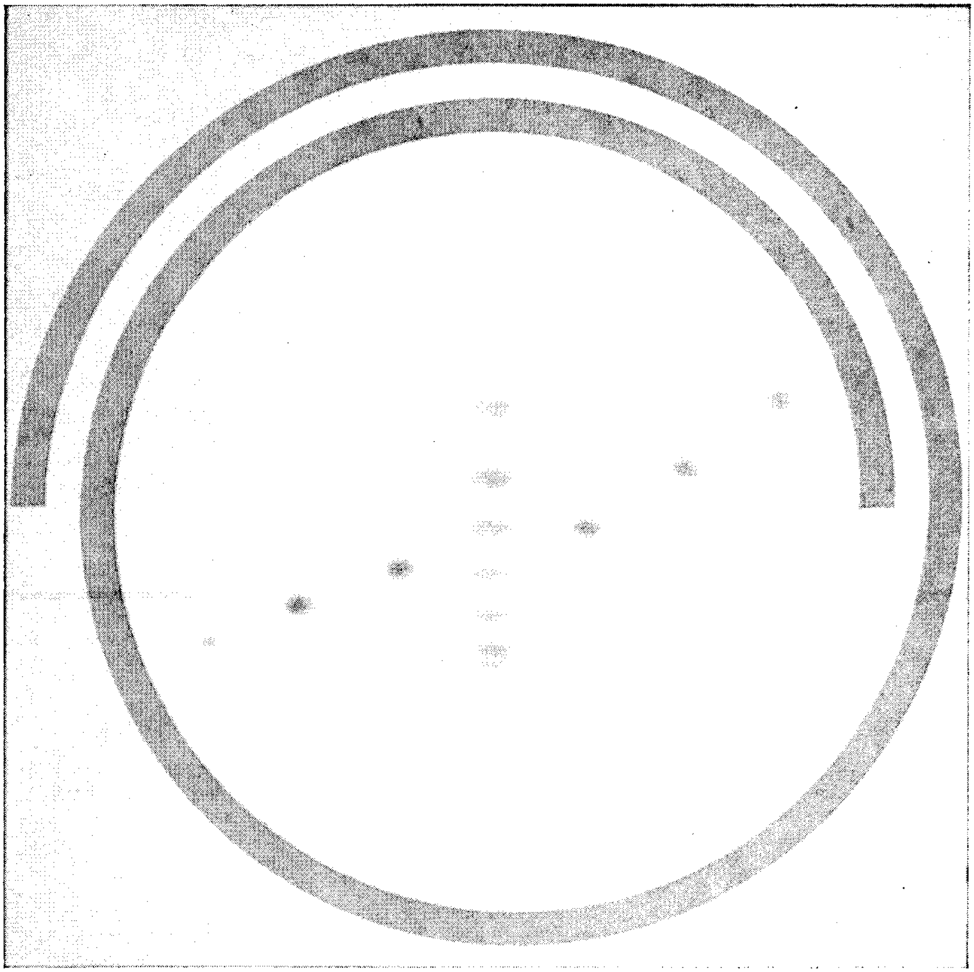

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ARNE TISELIUS

1902–1971

Arne Tiselius was born in Stockholm on August 10, 1902, but he grew up in Göteborg where he also went to school. After qualifying as a student he attended the University of Uppsala where he received his master's degree in 1924. He commenced his postgraduate studies in 1925 as a pupil of Theodor (The) Svedberg. Together with the late Ole Lamm he improved the ultracentrifuge technique by introducing refraction index shifts as a method of observing the sedimentation rate. Encouraged by Svedberg he started to study electrophoresis, and in 1930 he defended, with honors, a thesis entitled *The moving boundary method of studying the electrophoresis of proteins.* He discovered that serum proteins were heterogeneous and became aware of the importance of mild methods for the separation of proteins. In 1934–1935 he received a grant from the Rockefeller Foundation to study adsorption phenomena at Princeton University with Hugh S. Taylor. These studies proved to be important when, later, different chromatographic techniques were developed at his own department of biochemistry. Frontal analysis and the displacement method were developed with Stig Claesson and reversed-phase chromatography was published in 1951 with Kritchevsky. Nowadays probably gel filtration, discovered by his pupils Jerker Porath and Per Flodin, is the most widely used of these separation methods. Among his many research associates who visited his laboratory from abroad can be mentioned A. J. P. Martin and R. L. M. Synge. In 1948, Professor Tiselius was awarded the Nobel Chemistry Prize for his research on electrophoresis and adsorption analysis and especially for his discoveries concerning the complex nature of the serum proteins. Even when his department was internationally recognized as a centre for the development of methods for biochemical analysis, he also encouraged other aspects of biochemistry such as enzyme chemistry and microbiology and he took an active part in the establishment of EMBO (European Molecular Biology Organization). Several of his former pupils now have their own chairs of physical chemistry, biochemistry or microbiology. When he retired in 1968 Porath became his successor.

Many famous universities awarded him honorary doctorates: Paris in 1948, Cambridge in 1949, Bologna in 1955, Glasgow in 1956, Madrid in 1957, Oxford in 1958, Oslo in 1961, Lyon in 1962, St. Peter in 1963, Berkeley in 1964, Ann Arbor in 1967 and Prague in 1969. He also received several medals including the gold medal of the Franklin Institute and the Messel medal.

Professor Tiselius became a member of the Swedish Royal Academy of Sciences in 1939 and was its President from 1956 to 1957. He was also a member of the academies of many other countries. He had been a member of the Nobel Committee for Chemistry of the Royal Academy of Sciences since 1946 and Chairman of this committee since 1965. He served as Deputy Chairman of the Board of Directors of the Nobel Foundation from 1947 to 1960 and as Chairman from 1960 to 1964. He was also Director of the Nobel Institute from 1968. Professor Tiselius was largely responsible for the initiation of the Nobel Symposia, the first of which was held in 1966, and he

Arne Tiselius

was a member of the Nobel Foundation Symposium Committee. He took a special interest in those symposia concerned with chemical problems. At the last one, *The Changing Chemistry of the Oceans*, held in August 1971 outside Göteborg, Professor Tiselius stressed that reading and writing are not enough and that personal contacts deepen and widen perspectives. Professor Tiselius was very active in both Swedish and international organizations. He was President of IUPAC 1951–1955 and the first chairman of the Swedish Natural Science Council 1944–1950. He was chairman of the granting committee of the Swedish Cancer Fund and scientific adviser to the Wallenberg Foundation. He also took part in the creation of a scientific advisory board to the Swedish Government.

Professor Tiselius enjoyed more confidence than any other chemist in Sweden, not only from other scientists, research organizations, academies and the Nobel Foundation, but also from government authorities, and he used his great influence in a very broad-minded way. Although he always tried to improve the situation for basic natural science, he also stressed that scientists should take interest in the applications of their results and feel their responsibility for future development. Professor Tiselius took an active part in the Pugwash movement and he organized the Nobel Symposium *The Place of Value in a World of Facts.* His sudden death on October 29, 1971 was a great loss to Swedish science as well as to his friends and admirers all over the world.

David Dyrssen (Göteborg)

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CALIBRATION METHODS AND INSTRUMENTATION FOR OPTICAL ^{15}N DETERMINATIONS WITH ELECTRODELESS DISCHARGE TUBES

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The uses of nitrogen-15 as a tracer for the behaviour of nitrogen in agriculture are increasing rapidly. One obstacle to this development has been that the usual method of determining stable isotope concentration is by mass spectrometry, which is a relatively expensive and exacting technique. An alternative method of determining nitrogen-14/15 ratios is molecular emission spectroscopy, for bands in the electronic-vibrational spectrum of the nitrogen molecule show an isotope shift[1-5]. Optical spectrometers of reasonable resolution can be adapted relatively cheaply[6,7] for nitrogen-15 work, but it is only recently that a commercially available apparatus has appeared on the market (at a price very considerably below that of a mass spectrometer). A further advantage of the optical method is that very small samples can be measured. As little as 0.2 μg of total nitrogen is sufficient to obtain nitrogen-14/15 ratios[8], so that compounds separated by, for example, analytical chromatography are readily measurable.

As interest in the optical method for nitrogen-15 is increasing, it seemed worthwhile to investigate the suitability of commercially available components of the assembly so that in the case of adaptation of an emission spectrograph, the minimum amount of home-made equipment must be constructed. For this purpose, different commercially available antennae and resonance cavities for the electrodeless excitation of the nitrogen sample were compared with respect to their stability, the fitting of the discharge tubes and the cooling possibilities. At the same time, the opportunity was taken to study the methods of evaluation of the spectra to determine the nitrogen-14/15 ratios for the whole range of nitrogen-15 concentration (0.365 % (natural) to 97 % N).

In all these measurements, the electronic transition system $C(^3\Pi_u) \leftrightarrow B(^3\Pi_g)$ of the $2 \rightarrow 0$ transition was used, when the $^{14}N_2$ band head has a wavelength of 297.7 nm, the $^{14}N^{15}N$ band head 293.3 nm and the $^{15}N_2$ band head 298.9 nm.

EXPERIMENTAL

Apparatus

Measurements were carried out with a Hilger Watts quartz spectrograph E 742 modified into a spectrometer, equipped with a photomultiplier RCA 1P28, automatic scanning and recording[6,7]. A systematic investigation showed that the optimal conditions for resolution, light intensity and signal-to-noise ratio were obtained with

9-mm length and 0.075-mm width for the entrance slit and 0.04-mm width for the exit slit. All measurements were made with these settings.

For excitation of N_2 in glass tubes by the electrodeless discharge a previously described[6] microwave generator with a 100-Mc, 50-W output was used as one of the excitation sources. In order to investigate the possibilities of commercially available devices, a microwave power generator (Raytheon, Model PGM-10) with 2450 Mc, 85 W output was used. It was matched with 4 devices for transferring the energy: (*a*) Antenna A from Raytheon, (*b*) Antenna E from Raytheon, (*c*) Evenson-type $\frac{1}{4}$ wave cavity, and (*d*) Broida-type $\frac{3}{4}$ wave cavity.

Samples of known ^{15}N content used for this work were first determined with a Hitachi RMU6D mass spectrometer.

Sample preparation tubes

Three different types of tubes shown (Fig. 1) were used in the optical determination of ^{15}N.

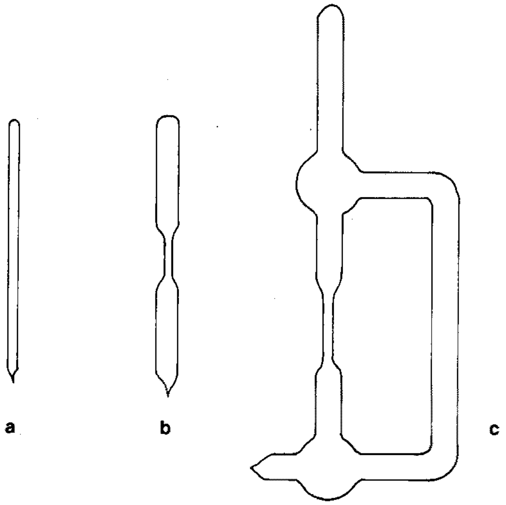

Fig. 1. Three different discharge tubes. (a) Quartz tube: 100 mm length, o.d. 4 mm, wall thickness 1 mm. (b) Uviol-glass tube: 100 mm length, o.d. 8 mm, wall thickness 1 mm. (c) Standard tubes delivered by Statron.

1. A quartz tube of about 0.26 ml volume[8]. It is mainly used for small samples containing 1–2 μg of total nitrogen. Nitrogen gas is released by combustion at 850° in vacuum with a copper oxide wire and a highly activated calcium oxide briquet[7]. The life of the tube is rather short depending on the nitrogen gas pressure; at 2–3 Torr it is about 30 min.

2. An Uviol-glass ampoule[9] of 2.2 ml volume prepared as described previously[10], and containing 3.5 Torr N_2 and a calcium oxide briquet to absorb any water and carbon dioxide. This tube is preferable as a standard tube because its life is at least 5 h.

3. This tube was only tested for its fitting into the different antennae and cavities and for its excitation, because it served only to contain standard samples of known nitrogen-15 content, as supplied with the commercially available nitrogen-15 spectrometer (Statron, Leipzig, DDR). It was not used to contain experimental samples.

High-frequency excitation sources

To test the antennae and cavities under the same conditions, three Uviol tubes filled with nitrogen gas of 0.365, 0.569 and 1.383 % ^{15}N abundance were measured on 4 different days. Each day, 8 determinations were made on each tube with the 5 different assemblies (*i.e.* the IAEA generator and the Raytheon generator with the four different antennae and cavities). The discharge was initiated with a Tesla coil vacuum tester. The samples were cooled during the measurements with compressed air so that the temperature during the discharge did not exceed 50°. This reduces the Döppler broadening of the bands[8] and gives the tubes a longer life. For the IAEA generator, air cooling was built into the design but in the other cases, a flexible plastic tube was used to direct an air-jet onto the sample.

RESULTS

The suitability of the various devices for the 3 types of specimen tubes is given below. One phenomenon was noticed, however, with all methods of excitation of the nitrogen gas. When the energy of the Raytheon microwave generator supplying power to the antenna and cavities was increased above the level found suitable for analysis, the light intensity and its concomitant signal from the spectrometer showed a negligible increase. The result of the increased power was to cause the plasma to expand further into the sample tube. The lowest energy level for analysis was about 50–100 % higher than the minimum energy required for maintaining the discharge. As the IAEA generator has a fixed power (50 W) this effect could not be investigated.

The *IAEA generator* was suitable only for tubes (a) and (b) (Fig. 1). The plasma was in the middle of the tube (the restricted part of type b) yielding a high signal. The mechanical support of the tubes was obtained merely by inserting them in the generator; the air-jet was built into the apparatus and initiation of the discharge was easy.

With *antenna A* all 3 types of tubes could be measured, but the gas could be excited only in the top part of the tubes, causing a lower signal for types (b) and (c) (25–30 % of a); 13 W was the analysing power. The mounting of tube and air-jet was simple, as was the starting of the discharge.

With *antenna E* only tubes (a) and (b) could be excited; in type (b) the plasma stayed only in the top part of the tube giving similar results to those of antenna A. Some difficulties were experienced with the cooling and with holding the tubes in position; 13 W were used for analysis. The initiation was sometimes rather difficult.

The *Evenson resonant cavity* gave trouble in only one respect. It was sensitive to power fluctuations from the generator with the result that tuning of the cavity was a little critical. It would be ideal with a stabilized power supply. Again, 13 W sufficed for analysis.

All 3 tubes could be inserted in the *Broida resonant cavity* but the plasma formed only in the top part of the tubes. The mechanical attachment of sample tubes and their cooling was easy, but the start of the discharge was sometimes difficult. Even when running on 40 W, the signal was only 25 % of that from the IAEA generator.

The results of the analysis of three different nitrogen-15 samples are shown in Table I. It can be seen that the results are accurate by comparison with the mass-spectroscopic values. All five systems have acceptable precision for samples from

TABLE I

COMPARISON OF THE RESULTS FOR 3 SAMPLES OBTAINED WITH DIFFERENT EXCITATION SOURCES (IAEA generator 100 Mc, Raytheon 2450 Mc)

Excitation source	*% ^{15}N abundance (mean over 4 days)*	*Relative standard deviation of a single measurement (%)*	*Error relative to mass. spec. values (%)*
IAEA generator	0.359	2.1	1.6
	0.563	1.3	0.9
	1.381	0.8	0.1
Raytheon antenna A	0.376	3.9	3.0
	0.580	3.7	1.9
	1.359	0.8	1.7
Raytheon antenna E	0.372	2.7	1.9
	0.584	1.9	2.6
	1.401	2.4	1.2
Evenson cavity	0.363	4.1	0.5
	0.558	1.6	1.9
	1.361	1.4	1.6
Broida cavity	0.377	2.5	3.3
	0.585	2.6	2.8
	1.414	1.7	2.2

agricultural field experiments. The precision of results obtained with the various antennae and cavities powered by the Raytheon generator was not so good as those from the specially built generator but this is probably due to the fact that the former was an instrument not intended for this purpose (but for therapeutic use) and was without special stabilization, whereas the IAEA generator was designed with stability of power.

EVALUATION OF SPECTRA

The output signal from the spectrometer, proportional to the intensity of the light falling on the photomultiplier, is plotted on an automatic chart recorder against the wavelength of the light. The height of the peaks obtained is a measure of the relative concentrations of the three types of nitrogen molecules $^{14}N^{14}N$, $^{14}N^{15}N$ and $^{15}N^{15}N$. Two effects, however, make direct estimates of concentrations difficult, and the method of calculation of results from the recordings has been approached empirically.

The structure of the molecular band spectrum consists of a sharply defined band head behind which are a series of closely spaced lines (which in the IAEA instrument are not resolved) making up the band. For a given electronic-vibrational transition, all the possible transitions between rotational levels together give rise to a single band. In the case of nitrogen, a band consists of 2 series of lines called the P and the R branches. The band head is formed by the P branch where the rotational fine structure lines are very close together (Fortrat parabola)[11], followed by an R branch which consists of fewer lines resulting in a lower intensity. This is illustrated in Fig. 2

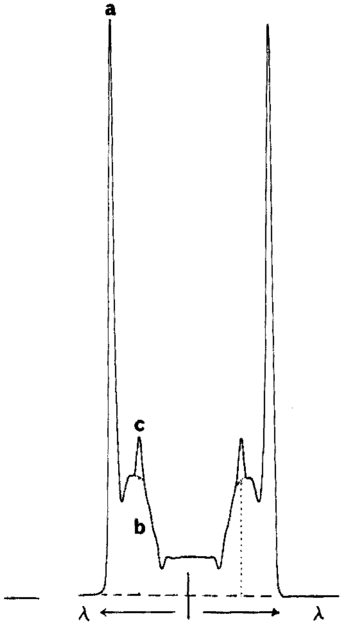

Fig. 2. Spectrum of a 97 % ^{15}N abundance sample between 299.5 nm and 297.4 nm. (------) Background of $^{15}N^{15}N$ peak; (......) 20 % of $^{15}N^{15}N$ peak as a correction for $^{14}N^{15}N$ peak height; (a) P branch of $^{15}N^{15}N$ band (band head); (b) R branch of $^{15}N^{15}N$ band; (c) P branch of $^{14}N^{15}N$ band (band head).

which shows the spectrum of a 97 % ^{15}N sample. The large sharp peak is the band head and P branch of $^{15}N^{15}N$ followed by a lower, broader peak which is the R branch. Superimposed on this is the small sharp peak which is the P branch of the small amount of $^{14}N^{15}N$ present in the sample. Its R branch is not visible. Thus the R branch of $^{15}N^{15}N$ influences the height of the P branch of $^{14}N^{15}N$ and similarly the R branch of $^{14}N^{15}N$ will interfere with the measurement of the P branch of $^{14}N^{14}N$. The extent of interference will of course depend on the relative concentrations of the molecules. From Fig. 2 it can be seen that the peak of $^{14}N^{15}N$ is raised above background by about 20 % of the height of the previous $^{15}N^{15}N$ peak. From many samples of known composition, the background from the R branch was found to be 20 ± 1 % of the previous peak (P branch).

The second difficulty with the present instrument arises when a low-intensity peak sits on the sharply falling shoulder of its neighbouring and much more intense peak (*e.g.* Fig. 3a). To determine the relative effects of the two influences and to arrive at the best empirical method for evaluating peak heights, 35 standard samples from 0.365–97 % ^{15}N abundance were measured by the mass spectrometer and by emission spectrometry. The optical spectra were then evaluated by various methods and compared with the mass-spectroscopic values.

In the electrodeless discharge, the following equilibrium is established, *viz.*

$$2\ ^{14}N^{15}N \rightleftharpoons {}^{14}N_2 + {}^{15}N_2$$

and the equilibrium constant, K_{eq}, is given by $[29]^2/[28][30] = 4$. Hence ^{15}N contents can be calculated from the concentration of two of the molecular types. Consequently

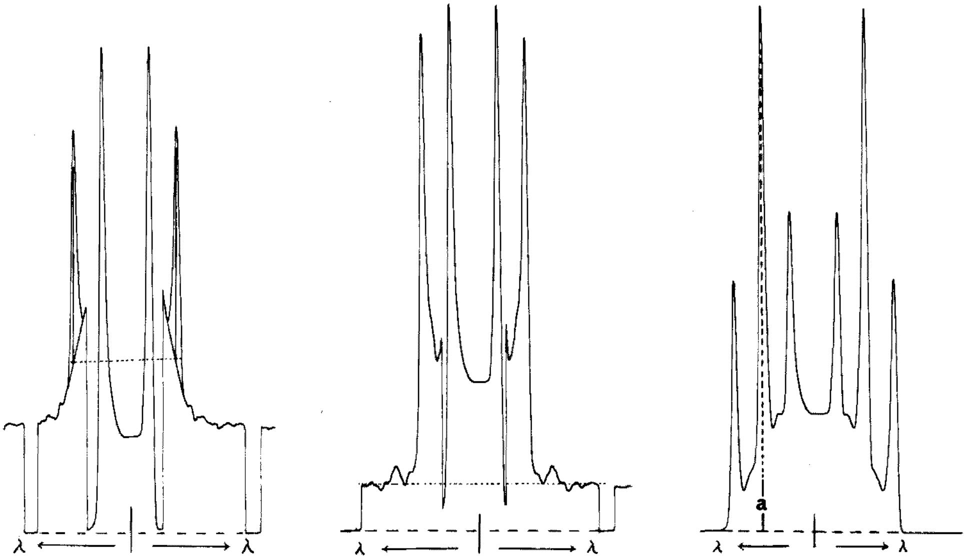

Fig. 3. Spectra of different ^{15}N abundances between 299.5 and 297.4 nm. (a) Natural abundance: (------) Background for $^{14}N^{14}N$ peak, (......) background for $^{14}N^{15}N$ peak, (——) interpolation of the background under the $^{14}N^{15}N$ peak. (b) 4.91% ^{15}N: (------) Background for $^{14}N^{14}N$ peak, (......) background for $^{14}N^{15}N$ peak. (c) 51.7% ^{15}N: (------) Background for $^{15}N^{15}N$ and $^{14}N^{15}N$ peak, (—a—) 20% of $^{15}N^{15}N$ peak as a correction for $^{14}N^{15}N$ peak height.

each sample was evaluated from an appropriate measure of the peak heights of the $^{14}N^{14}N$ and $^{14}N^{15}N$ bands or the $^{14}N^{15}N$ and the $^{15}N^{15}N$ bands depending on the concentration range. In some cases where all three peak heights were measurable with reasonable accuracy, both methods were used. In this case, the equilibrium constant K_{eq} was also calculated and good agreement with the theoretical value of 4 obtained.

The methods of evaluation given below apply to the apparatus available here, with a reciprocal linear dispersion equal to 2 nm mm^{-1}. With the lower dispersion of 4 nm mm^{-1}, such as is achieved in the commercially available Statron NOI-4 nitrogen analyser, such methods are not possible and a calibration curve of peak height against known nitrogen-15 concentrations (from reference samples) must be made.

Of the various possible methods of calculation, none was suitable for the entire range of concentration of nitrogen-15. The basis of the five best are given below, starting with low nitrogen-15 containing samples.

1. The vertical height of the $^{14}N_2$ peak above the background (VHAB) and the vertical height of the $^{14}N^{15}N$ peak above the interpolated background of the shoulder of the $^{14}N_2$ peak (see Fig. 3a).

2. The VHAB of the $^{14}N_2$ peak and the VHAB of the $^{14}N^{15}N$ peak. (Where peaks were recorded with different amplifications, the background of the peak was taken for the appropriate amplification. See Fig. 3b. The peak height was subsequently corrected for the amplification factor.)

3. The VHAB of the $^{14}N^{15}N$ and the height of the $^{15}N_2$ peak above the linear interpolation of the shoulder of the $^{14}N^{15}N$ peak.

4. The VHAB of the $^{14}N^{15}N$ peak and the VHAB of the $^{15}N_2$ peak.

TABLE II

COMPARISON OF MASS SPECTROMETRIC WITH EMISSION SPECTROMETRIC VALUES

Mass spec. values	*Emission spec. Method* 1	*Relative error*	*Mass spec. values*	*Emission spec. Method* 2	*Relative error*	K_{eq}	*Mass spec. values*	*Emission spec. Method* 4	*Relative error*	K_{eq}	*Mass spec. values*	*Emission spec. Method* 5	*Relative error*
0.359	0.360	0	4.07	4.21	+3.4		13.50	13.9	+2	4.2	51.5	52.6	+2
0.463	0.468	+1.5	4.66	4.75	+2.0		18.11	18.3	+1.5	4.0	51.7	52.9	+2.5
0.572	0.577	+1.0	4.67	4.67	0		20.81	21.6	+3.8	4.1	53.6	53.7	0
0.772	0.768	−0.5	4.68	4.81	+2.5		20.89	21.4	+2.9	4.0	59.5	60.9	+2.5
0.885	0.889	+0.5	4.91	5.06	+3.0		27.0	27.0	0	3.9	69.6	71.0	+2.0
1.171	1.188	+1.5	6.72	6.71	0	3.9	30.5	29.2	−4.5	4.1	83.8	85.5	+1.5
2.129	2.10	−1.5	8.83	8.82	0	4.1	33.5	33.9	+1.0	4.0	89.6	90.1	+0.5
2.404	2.34	−3.0	10.86	10.80	−0.5	4.1	35.9	36.5	+1.5	4.3	96.0	95.0	−1.0
3.024	2.94	−2.5	13.50	13.0	−3.7	4.0	44.3	44.2	0	4.3	97.0	95.5	−1.5

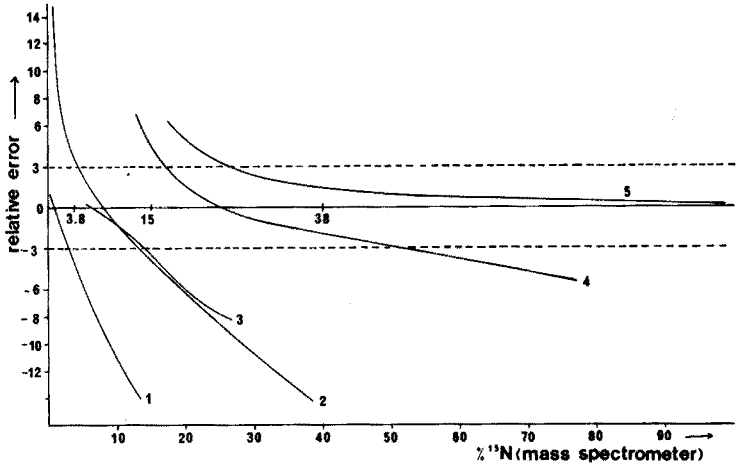

Fig. 4. The relative errors of emission spectrometric measurements of the 5 different spectrum evaluation methods against the mass spectrometric values taken as standards.

5. The VHAB of the $^{14}N^{15}N$ peak reduced by 20% of the peak height of the $^{15}N_2$ peak and the VHAB of the $^{15}N_2$ peak (Fig. 3c).

The relative errors of the spectroscopic measurements in comparison with the mass spectrometric values taken as standard are illustrated in Fig. 4; detailed results are given in Table II. Experience has shown from samples measured in the course of a year that a relative standard deviation of ±3% for a sample determination is obtainable. This value was therefore taken as the limit of acceptability of the various methods for interpretation of nitrogen-15 content. Up to about 3.8% ^{15}N method 1 is satisfactory. Above this, the increasing size of the R branch of the $^{14}N^{15}N$ peak and the difficulty of interpolating the $^{14}N_2$ peak background make this method too unreliable and method 2 gives much better results up to about 14–15% ^{15}N. Method 3 is adequate over a limited portion of this range but it is difficult to use in the lower ^{15}N range (where extrapolation (Fig. 4) would suggest it would be better than method 2) because the $^{15}N_2$ peak is very small. The region 14–17% is not properly served by any method but at about 17%, method 4 is satisfactory upto about 50%. However, above 27%, method 5 is also satisfactory and extends up to 100% ^{15}N. The various ranges of reliability of the 5 methods reflect the relative influences of the two factors on the estimations of peak height.

CONCLUSIONS

Of the commercially available equipment to excite the nitrogen samples, the Raytheon PGM-10 microwave generator and antenna A (Raytheon) or the Evenson resonance cavity to transmit the power give satisfactory results although the generator is not designed for analytical purposes and is not specially stabilized. An improvement of stability should give a better standard deviation.

From an empirical study of the evaluation of the emission spectra of $^{14}N^{15}N$ gas, no one method is satisfactory over the entire range of nitrogen-15 concentration. For the range 0.36–3.7% ^{15}N, method 1 is satisfactory, from 3.7–15% method 2 and from 15–50 % method 4 can be used although the errors may exceed ±3 % in the case of both methods 2 and 4 in the range 14–17 %. Method 3 covers too small a region to be useful and in any case the results agree with method 2. From 27–100 % ^{15}N method 5 is satisfactory, particularly in the range above 40 % ^{15}N.

The authors would like to thank Dr. G. B. Cook for his advice and support in this work.

SUMMARY

For the electrodeless excitation of nitrogen in discharge tubes a commercially available microwave power generator as well as two antennae and two resonant cavities were compared with respect to their stability, the fitting of the discharge tube and the cooling possibilities. Different methods of evaluation of the spectra to determine the nitrogen-14/15 ratio for the whole range of nitrogen-15 concentration 0.365 % (natural) to 97 % were studied empirically and 4 methods were recommended for different ranges of concentration.

RÉSUMÉ

On examine les possibilités de détermination de l'azote-15, à l'aide de tubes à décharge sans électrode. On propose diverses méthodes d'évaluation du rapportazote-14/15, pour différents domaines de concentration.

ZUSAMMENFASSUNG

Für die elektrodenlose Anregung von Stickstoff in Entladungsröhren wurden ein handelsüblicher Mikrowellen-Generator sowie zwei Antennen und zwei Hohlraumresonatoren verglichen im Hinblick auf ihre Stabilität, die Anpassung der Entladungsröhre und die Kühlmöglichkeiten. Es wurden verschiedene Methoden der Auswertung der Spektren für die Bestimmung des Stickstoff-14/15-Verhältnisses im gesamten Stickstoff-15-Konzentrationsbereich von 0.365 % (natürlich) bis 97 % empirisch untersucht, und vier Methoden werden für verschiedene Konzentrationsbereiche empfohlen.

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ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

PART X. THE DETERMINATION OF NICKEL WITH AN UNENCLOSED ATOM RESERVOIR*

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(Received 8th November 1971)

Since the first description of the carbon filament atom reservoir in atomic absorption and fluorescence spectroscopy[1], several papers from this laboratory have reported its application to volatile and involatile metals, as well as studies of matrix effects.

In a recent paper by Dipierro and Tessari[2] the determination of nickel by atomic absorption spectroscopy is described, but the apparatus used closely resembles that originally devised in this department[1]. The work described below shows how the absolute detection limit of $1 \cdot 10^{-9}$ g reported by the above authors can be improved by using the modified carbon filament, and how the inevitable matrix effects can be suppressed to an acceptable level by means of careful collimation of the light beam before entry into the monochromator.

EXPERIMENTAL

Apparatus

A modified Perkin-Elmer 290B atomic absorption spectrophotometer incorporating a Littrow grating monochromator was used. This instrument had been used previously[3] with no modification apart from the substitution of the carbon filament atom reservoir for the standard nebulizer and burner, and satisfactory results were obtained during the determination of copper, silver, zinc, cadmium and lead. In the case of nickel, however, the absorption peak half-width is of the order of 0.4 sec and the response of the Perkin-Elmer 290B amplifier was found to be too slow to enable the measurement of such a transient signal. In view of this a fast-response d.c. system was employed.

The source was a Sullivan and Walsh high-intensity nickel hollow-cathode lamp (ASL). This was powered by a Techtron AA4 power supply and booster unit. The lamp was normally operated at a primary cathode current of 25 mA and a secondary current of 500 mA. These were the highest currents recommended by the manufacturer.

The standard Perkin-Elmer 290B photomultiplier was used and the output of this was connected directly to a Telequipment storage oscilloscope, type TD51. This incorporated a "type-K" amplifier which has a rise time to full-scale deflection of only 70 nsec.

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The incident radiation from the lamp was focussed by means of two quartz lenses of approximate focal length 70 mm, to a point immediately above the carbon filament. The collimator was placed about 10 mm after the filament and the radiation was focussed and directed by means of a third lens and two mirrors on to the monochromator entrance slit. This instrumental set-up is shown in Fig. 1.

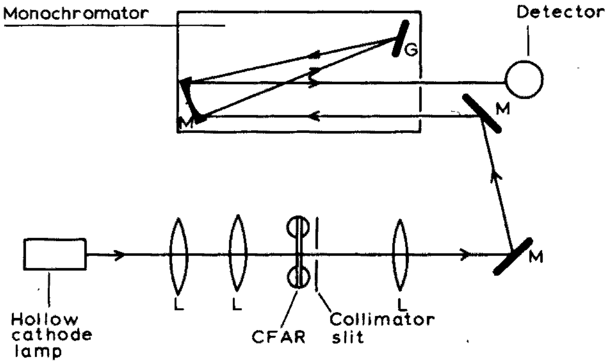

Fig. 1. Optical arrangement. (L) Lens; (M) mirror; (G) Littrow grating.

For the best detection limit, *i.e.* least background "noise", it was found that the EHT power supply to the photomultiplier should be set at the maximum possible and the monochromator entrance slit should be as wide as possible (to give a bandpass of 2 nm). In this way, the minimum gain was required on the type-K amplifier.

Reagents

All reagents were of analytical grade. Water was glass-distilled and then deionized with a cation-exchange resin in the H^+ form. The water thus purified was found to contain no measurable nickel contamination.

During previous work it had been found necessary to treat all glassware with "Repelcote" in view of loss by surface adsorption from the very dilute solutions employed. In the case of nickel, solutions were usually less dilute and it was found that provided solutions were freshly prepared each day, treatment with "Repelcote" was not generally necessary.

For the preparation of all nickel solutions, nickel chloride hexahydrate was used.

Measurement technique

Preliminary experiments showed the following technique to give the best sensitivity, detection limit and reproducibility.

The monochromator was tuned to receive the nickel line at 232.0 nm and the filament shielding-gas (argon) was allowed to flow at a rate of 3.6 $l\ min^{-1}$. The aqueous sample (5 μl) was placed by means of a Drummond micro-pipette into a small recess carved in the filament. The following time cycle was then followed:

At time (t) = 0, the filament was switched on at low power (about 1.5 V). This evaporated the water from the sample without sputtering.

At $t = 10$ sec the power was switched off.

At $t = 15$ sec the power was switched on at 12 V. This gave a filament temperature of about 2400° after 1 sec and was sufficient to atomize the nickel.

At $t = 16$ sec the power was switched off and the peak height was measured on the oscilloscope.

At $t = 45$ sec another sample was placed on the filament.

At $t = 50$ sec the cycle was repeated.

Thus, with this technique it was possible to carry out one determination every 50 sec.

When this procedure was followed, it was found that if the filament voltage was turned on again after the sample had been vaporized, no absorption peak was obtained, *i.e.* all of the nickel was removed from the rod during a determination and thus there was no memory effect.

RESULTS AND DISCUSSION

Effect of filament voltage on signal

It would be expected that as the voltage, and hence filament temperature, increased the rate of atomization of the nickel would also increase. This should result in the absorption peaks becoming narrower and higher as the temperature increases. It can be seen from Fig. 2 that this did in fact occur, and hence the optimal voltage was the highest attainable (12 V). Measurements of the filament temperature with an optical pyrometer showed that at this voltage, the temperature reached 2400° 1 sec after switching on.

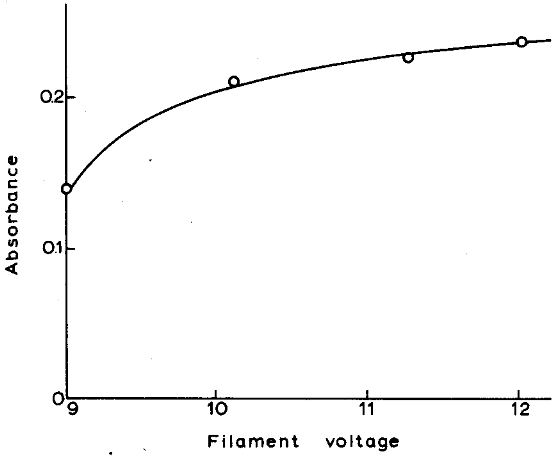

Fig. 2. Variation of absorbance with filament voltage (5 ng Ni at 232.0 nm).

In much of the previous work on carbon filaments, a quite considerable drop in peak height was observed at the higher voltages, and this was generally attributed to the rate of atomization being so high at these temperatures that the detection/amplification systems in use were not of sufficiently fast response to follow these signals. The speed of response of the present detection/amplification system, however, was such that the fastest signals could easily be seen.

Effect of shielding gas flow rate on signal

When the argon flow rate was plotted against absorbance, the curve shown in Fig. 3 was obtained. It can be seen that the optimal flow rate was 3.6 l min^{-1}.

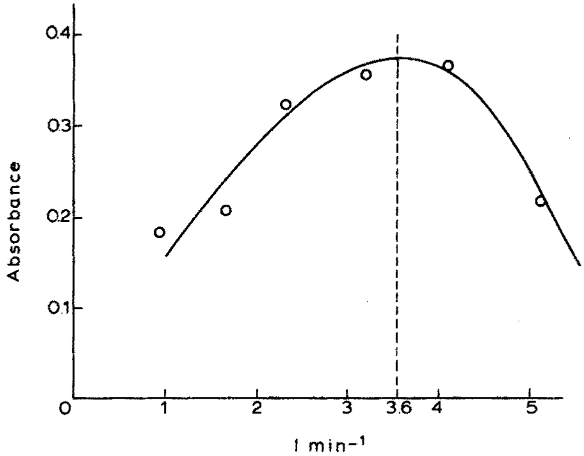

Fig. 3. Effect of argon flow rate on absorbance (5 ng Ni at 232.0 nm).

TABLE I

WAVELENGTHS FOR NICKEL

Wavelength (nm)	*Ground state energy*[4] *(eV)*	*Absorbance*[a]	*Noise (absorbance units)*
232.0	0	0.257	0.014
298.2	0.11	0.046	0.012
300.3	0.03	0.052	0.012
305.1	0.03	0.058	0.007
352.4	0.03	0.041	0.008

[a] For 5 μl × 1 p.p.m. of nickel chloride solution (*i.e.* 5 ng Ni).

Calibration curves and detection limits

Several wavelengths were examined from the point of view of sensitivity and background noise at a concentration of 1 p.p.m. nickel. The results are summarized in Table I. It is obvious from these results that the line at 232.0 nm shows by far the best sensitivity at this concentration, even though the background noise is a little higher than in the other cases.

Several calibration curves were plotted at this wavelength, covering various concentration ranges (5-μl aliquots in every case) and the curve for the optimal working range, *viz.* 0.05–2.00 p.p.m., is shown in Fig. 4. It can be seen that although this graph is almost linear up to about 0.8 p.p.m., it then begins to curve with increasing concentration; almost maximal absorbance was attained at about 10 p.p.m., when the curve had become nearly parallel to the *x*-axis. In order to extend the maximal concentration, the less sensitive lines were examined, and that at 305.1 nm was found to give a greater linear working range without levelling off until a con-

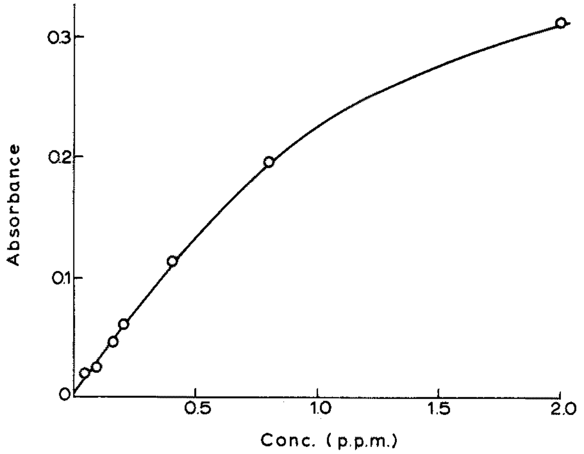

Fig. 4. Analytical calibration curve at 232.0 nm.

TABLE II

DETECTION LIMITS, SENSITIVITIES AND WORKING RANGES
(Sample volume = 5 μl)

Wavelength (nm)	*Detection limit*		*Sensitivity (g)*	*Working range (p.p.m.)*
	p.p.m.	*g*		
232.0	0.04	$2.0 \cdot 10^{-10}$	$9.5 \cdot 10^{-11}$	0.05–2.0
305.1	0.16	$8.0 \cdot 10^{-10}$	$5.4 \cdot 10^{-10}$	0.4–10.0

centration of 50 p.p.m. The results are summarized in Table II. The detection limit is defined as that concentration at which the peak height is equal to twice the r.m.s. of the background noise. Sensitivity is taken as the concentration (or absolute amount in this case) of nickel which would produce a 1% change in absorption over the linear part of the calibration curve.

The detection limit at 232.0 nm ($2 \cdot 10^{-10}$ g) is similar to that originally obtained with a Techtron AA4 atomic absorption spectrophotometer[5] ($3 \cdot 10^{-10}$ g), when the analytical line at 341.5 nm was employed. The working ranges are also almost identical and it can thus be concluded that both of these lines will be of equal merit with regard to both sensitivity and detection limit.

The non-linearity of the calibration graphs can be explained largely by the fact that the incident light beam can never be focussed at the filament to such an extent that the entire beam will be concentrated into the atomic cloud. In this case the maximum absorption attained (at 232.0 nm) was just below 70% (absorbance of 0.523), and this value was approached asymptotically as the concentration was increased. It can be seen from Fig. 5 that a calibration curve showing better sensitivity (steeper gradient) will thus show greater curvature.

Reproducibility

Aliquots (5 μl) of a 1-p.p.m. nickel solution were repeatedly analysed under

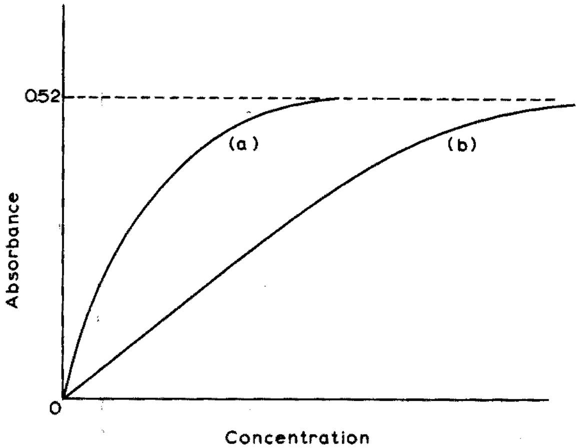

Fig. 5. Illustration of effect of sensitivity on curvature of calibration graphs. (a) Line of high sensitivity, *e.g.* 232.0 nm; (b) line of lower sensitivity and hence greater linear range, *e.g.* 305.1 nm.

optimal conditions. Eleven determinations gave a standard deviation of 3.1%. The reproducibility tended to be a little poorer than for the determination of volatile metals such as zinc, cadmium, magnesium, etc., and this can be largely attributed to the higher carbon filament temperatures required in the case of nickel. The rate of heating of the filament was critical, since slow heating resulted in the atomization being extended over a longer period. This produced a wider and hence lower absorption peak. It was found that unless the electrical contacts between the stainless steel electrodes and the carbon filament were very good, the rate of heating of the filament tended to vary slightly from one determination to another. This problem would, of course, be obviated by peak-area rather than peak-height measurements.

Origin of the signal

The possibility that the signals could be wholly or partly attributed to scatter was examined by studying a non-absorbing nickel line. The line at 338.1 nm (originating from a ground-state energy level of 0.423 eV[4]) was chosen as being sufficiently close to the absorbing line at 305.1 nm. Further, the nickel lamp was also replaced by a zinc hollow-cathode lamp and the line at 307.6 nm was examined. In neither case was any signal observed, confirming that the signals at the nickel absorbing lines originated purely from atomic absorption by nickel.

Interference studies

It was previously shown[6,7] that interferences occurred predominantly in the vapour phase, *i.e.* after the species present had left the filament surface, and also that the interferences were temperature-dependent. Since the highest temperatures occur closest to the filament surface, it was also found that interferences were least troublesome when a narrow collimator slit was placed immediately after the filament and arranged horizontally so that the atomic population was viewed very close to and immediately above the filament.

Preliminary experiments for nickel in the presence of interfering species tended to confirm these findings. Several horizontal slit-widths were used in the collimators and the narrowest tried, *viz.* 0.5 mm, not only showed the maximum suppression of interferences, but also gave the best sensitivity for the nickel determination. The optimal position for the slit was such that it was as close above the filament surface as possible.

A comprehensive study of interferences was made for this collimation system. In every case, a nickel solution of concentration 1 p.p.m. was used. Anionic interferents were studied at a range of concentrations from 10–10^5 p.p.m., whilst cationic interferents were studied at concentrations of 10, 10^2 and 10^3 p.p.m. Cationic interferences were added as the metal chloride in every case except vanadium, when ammonium metavanadate, dissolved in very dilute hydrochloric acid, was used.

It was found that the reproducibility of the absorption signal in the presence of interfering species was not as good as for pure nickel solutions. For this reason, all interferences, which are represented as percentage suppression of the absorbance of pure nickel, were rounded off to the nearest 5%. The results obtained are shown in Table III. The metals are tabulated in decreasing order of interference. It can be seen

TABLE III

PERCENTAGE SUPPRESSION OF ABSORBANCE OF 1 p.p.m. (5 ng) NICKEL BY ADDITION OF INTERFERING SPECIES

(Sample volume = 5 μl)

Interferent	*Compound used*	*Interference*				
		10 *p.p.m.* (50 *ng*)	10^2 *p.p.m.* (500 *ng*)	10^3 *p.p.m.* (5000 *ng*)	10^4 *p.p.m.* (50,000 *ng*)	10^5 *p.p.m.* (500,000 *ng*)
SO_4^{2-}	H_2SO_4	0	10	10	35	—
NO_3^-	HNO_3	0	5	10	30	30
F^-	HF	0	0	0	30	60
Cl^-	HCl	0	0	0	0	20
Cr(III)	$CrCl_3$	25	55	100		
Be	$BeCO_3$/HCl	20	25	35		
Sn(II)	$SnCl_2$	20	—	—	—	
Fe(III)	$FeCl_3$	10	50	80		
Mg	$MgCl_2$	10	40	60		
Mn(II)	$MnCl_2$	10	40	55		
Co(II)	$CoCl_2$	0	35	80		
Cu(II)	$CuCl_2$	5	30	80		
Al	$AlCl_3$	5	35	50		
Zn	Zn/HCl	5	15	40		
Ca	$CaCl_2$	5	20	35		
Rb	RbCl	0	10	30		
Cd	$CdCl_2$	0	10	30		
V(V)	NH_4VO_3/HCl	5	15	25		
K	KCl	0	10	20		
Na	NaCl	5	10	15		
Sr	$SrCl_2$	5	10	10		
Li	LiCl	0	5	10		
Hg(II)	$HgCl_2$	0	0	20		
Cs	CsCl	0	0	5		
Ba	$BaCl_2$	0	0	5		
Pb	$PbCl_2$	0	0	0		
Ti(IV)	$TiCl_4$	0	0	0		

that even at 10 p.p.m., Cr(III), Be, Sn(II), Fe(III), Mg and Mn(II) interfered significantly. A series of experiments involving improved collimation was initiated, for more selective viewing should reduce the interferences. Instead of using a simple horizontal slit of unlimited width, a second slit was placed in front of and perpendicular to the first. With these crossed slits a small rectangle was thus obtained. The following three cross-slit arrangements were examined: 0.5 × 2.0 mm, 0.5 × 1.0 mm and 0.5 × 0.5 mm.

It was found that the smallest collimator gave the best suppression of interference, but such selective viewing resulted in a loss of intensity of the radiation which reached the detector. A higher gain on the amplifier was thus required and this resulted in an increase in background noise. Hence the second arrangement (0.5 × 1.0 mm) was chosen as a compromise and it was found that the increase in background noise was within the acceptable limit. It can be seen from the results in Table IV that with this crossed slit collimator almost all of the interferences at a concentration of 10 p.p.m. could be reduced to an acceptable level.

TABLE IV

PERCENTAGE SUPPRESSION OF ABSORBANCE OF 1 p.p.m. (5 ng) NICKEL BY ADDITION OF INTERFERING SPECIES—IMPROVED COLLIMATION

(Sample volume = 5 μl)

Interferent	*Interference*		
	10 p.p.m. *(50 ng)*	*10^2 p.p.m.* *(500 ng)*	*10^3 p.p.m.* *(5000 ng)*
Cr(III)	10	50	55
Be	0	5	40
Sn(II)	20	—	—
Fe(III)	10	40	60
Mg	0	5	15
Mn(II)	10	40	60

It should be noted that the carbon filaments in general use were found to contain some nickel impurity. Normally this was so small that no significant contribution to the absorption signal occurred, but when cross-slits were employed a very small area just above the rod was being examined and this area was much richer in nickel than the larger area previously viewed. It was therefore very difficult to eliminate any contribution from this residual nickel, and spectroscopically pure carbon rods (Johnson Matthey Chemicals Ltd.) of 3.2 mm diameter were employed for these crossed slit experiments because they contained no significant amounts of nickel.

A feature of these interference studies is that there is a great tolerance for common anions and that elements which are difficult to atomize, *e.g.* Ti(IV), do not show abnormal matrix effects as they do in flame spectrophotometry.

Mechanism of interference

Attempts were made to correlate degree of interference with some physical properties of the interfering species, in order that a greater understanding might be obtained of the mechanisms by which interferences occur.

Those physical properties of the metal chlorides, and also of the pure metals, which were considered to be probable contributors to the degree of interference were examined. These were melting point, boiling point and, in the case of the metal chlorides, heat of formation.

The properties of the interfering compound were found to show no correlation whatever and this indicated that, generally, initial breakdown to the metal atom, *i.e.* variable atomization of compounds on the rod, is not one of the factors influencing interference. However, some correlations were evident when properties of the pure metals were plotted and it would appear that metals of low volatility, *i.e.* similar volatility to nickel, tend to interfere the most. Earlier work involving the atomic absorption and fluorescence of volatile metals tended to show that the more volatile foreign species caused the greater suppression of signal. This is contrary to the findings in the present case, but the earlier interference studies used broad field viewing when the influence of the more volatile elements, which tend to condense higher above the filament, would be more in evidence.

By viewing over a narrow area, immediately above the filament, it would be expected that chiefly those elements that are atomized at temperatures similar to the element being determined would show serious interference, and this is substantiated in the case of interferences on nickel. Also, if the foreign species has a high boiling point, it is liable to cause the more serious interference, because it is more likely to condense within the field of view, and hence occlude or cocrystallize the nickel.

Accordingly, selective viewing should always result in decreased interference, but less volatile metals such as nickel may still experience a greater degree of interference though not necessarily a larger number of interferences than easily volatilized species such as magnesium, zinc, cadmium, etc. It must be stressed, however, that the above conclusions are only based on generalizations, since the correlation between volatility and degree of interference is not particularly good. The mechanism of interference is complex and cannot be wholly attributed to any single physical property.

We are grateful to Laporte Industries Ltd. for assistance and support for this programme and also to the S.R.C. for the provision of a CAPS award for K.W.J. Thanks are also due to Mr. D. Alger of this department for his advice on electronic apparatus.

SUMMARY

The detection and measurement of nickel by atomic absorption spectroscopy with a carbon filament atom reservoir and a hollow-cathode lamp is described. Determinations were carried out at several wavelengths; the lowest detection limit of $2 \cdot 10^{-10}$ g (0.04 p.p.m.) was found at 232.0 nm. The effects of various interfering species were examined and it was shown how interferences could be minimized by restricting the viewing of the absorption signals to a small area immediately above the carbon filament. A study of the volatilities of the interfering species showed that the larger interferences could often be associated with metals which have a volatility similar to that of nickel.

RÉSUMÉ

On examine la détection et le dosage du nickel par spectrophotométrie d'absorption atomique avec réservoir atomique à filament de carbone et lampe à cathode creuse. Les déterminations sont effectuées à plusieurs longueurs d'ondes. On arrive à la limite la plus basse de $2 \cdot 10^{-10}$ g (0.04 p.p.m.), à 232.0 nm. L'influence de diverses substances est examinée.

ZUSAMMENFASSUNG

Der Nachweis und die Bestimmung von Nickel durch Atomabsorptionsspektroskopie mit einem Kohlefaden-Atomisator und einer Hohlkathodenlampe werden beschrieben. Die Bestimmungen wurden bei verschiedenen Wellenlängen ausgeführt; die niedrigste Nachweisgrenze von $2 \cdot 10^{-10}$ g (0.04 p.p.m.) wurde bei 232.0 nm erhalten. Die Einflüsse verschiedener störender Spezies wurden untersucht, und es wurde gezeigt, wie Störungen durch Beschränkung der erfassten Absorptionssignale auf einen kleinen Bereich unmittelbar oberhalb des Kohlefadens vermindert werden konnten. Eine Betrachtung der Flüchtigkeiten der störenden Spezies ergab, dass die grösseren Störungen häufig auf Metalle zurückgeführt werden konnten, deren Flüchtigkeit der von Nickel ähnlich ist.

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CHEMICAL AND SPECTRAL INTERFERENCES IN THE DETERMINATION OF COBALT IN IRON AND STEEL BY ATOMIC ABSORPTION SPECTROSCOPY

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Of the analytical methods commonly used for the determination of cobalt in iron and steel, no single method covers the full range of levels which can occur. A zinc oxide–α-nitroso-β-naphthol gravimetric procedure[1] is used for the low range (0.001–0.040% Co). For the high range (up to 15%) there is a choice of a photometric procedure with nitroso-R salt[2] or an ion-exchange–potentiometric titration procedure[3]. A procedure based on atomic absorption spectrophotometry (a.a.s.) would provide an attractive alternative to these, particularly for the low-range method which is tedious and time-consuming.

The determination of cobalt in steel by a.a.s. was first reported by McPherson *et al.*[4]. Results obtained on a range of low-alloy and stainless steel[5] gave no indication of interference effects. Sprague and Slavin[6] proposed a scheme of analysis for a number of elements in steel, including cobalt, by a.a.s. Although some of the cobalt results showed unsatisfactory agreement with certificate values, no interference study was undertaken. Ramirez-Muñoz and Roth[7] also determined cobalt in steel by a.a.s. They claimed good precision and satisfactory agreement with NBS values but the scope of their investigation was very limited. The Standards Association of Australia CH4 Committee on Sampling and Analysis of Ferrous Metals has investigated a draft method for the determination of cobalt in iron and steel by a.a.s. with a number of cooperating laboratories taking part. The results obtained on a range of low-alloy and alloy steels were unacceptable with regard to both accuracy and precision.

This paper describes a study made of some observed interference effects with a view to understanding and overcoming them. The use of the nitrous oxide–acetylene flame for the determination is proposed.

INTERFERENCES

A lean or oxidizing air–acetylene flame is normally recommended for the determination of cobalt by a.a.s.[8]. The difficulty of specifying and describing flames was recognized as a possible source of error and so an investigation was undertaken to determine the effect of flame type on both sensitivity and accuracy. Calibration standards containing pure iron and increasing concentrations of cobalt were prepared in three different acid media, hydrochloric acid (10% v/v), perchloric acid (10% v/v) and sulphuric–phosphoric acid (3%/3% v/v). Three standard steels, SRM 19g, BCS 335 and SRM 126b, each spiked with 0.300% Co, were similarly prepared in

TABLE I

RANGE OF FLAMES USED IN DETERMINING THE EFFECT OF FLAME TYPE ON SENSITIVITY AND ACCURACY OF THE DETERMINATION OF COBALT IN IRON AND STEEL (Figs. 1 and 2)

(The flow rotameter setting for air at 20 p.s.i. was held constant at 5.25)

Flame	*Flow rotameter settings*	*Flame description*
	C_2H_2 (11.5 p.s.i.)	
A	1.75	Blue inner cone (1.5 mm)
B	2	Blue inner cone (2 mm)
C	2.5	Blue inner cone (3 mm)
D	3	Blue inner cone (4 mm) surrounded by lighter hazy cone (8 mm)
E	3.25	Blue inner cone (4 mm) surrounded by lighter hazy cone (10 mm)

each acid medium. Absorbance readings were taken on all solutions in a series of air–acetylene flames ranging from lean or oxidizing in nature to fuel-rich or reducing (Table I). A 5-cm burner was used and the light beam was centered 5 mm above the top of the burner for all absorbance readings. The investigation was thus restricted to only one section of the flame.

The calibration curves plotted from the absorbance readings (Fig. 1) showed wide variations in slope. This was most pronounced in the sulphuric–phosphoric acid medium. These effects can be attributed to variations in the cobalt free atom population which could be brought about by variations in the degree of atomization, or to compound formation within the flame.

The results obtained on the three standard steels (Fig. 2) show that serious interference can occur, because of the presence of alloying elements, unless a fairly oxidizing air–acetylene flame is used. These interferences can result in either enhancement or depression and are influenced by the acid medium used. They can be attributed to further changes in the cobalt free atom populations relative to those present in the calibration series containing pure iron.

During this investigation it was noticed that blank absorbance readings were obtained on solutions of pure iron (Fig. 1). These readings were highest in oxidizing flames and were not evident in fuel-rich flames. An investigation of the cause of this blank was undertaken.

The emission from a hollow-cathode lamp was scanned in the region of the 240.7-nm cobalt line with a slit-width of 10 μm. The scan was repeated while an iron solution was aspirated into an oxidizing air–acetylene flame and absorption of all lines in the region was observed. The extent of the absorption of some of the lines is shown in Fig. 3. As solutions of nickel and of chromium were shown to absorb to a much lesser extent, it would be expected that alloy steels would have a smaller blank than plain carbon steels.

Background absorption has been attributed to a variety of causes in the past. In a theoretical consideration of the subject Koirtyohann and Pickett[9] concluded that while some light scattering by salt particles in the flame does occur, it is small and should be approximately the same for all wavelengths. They consider that some other

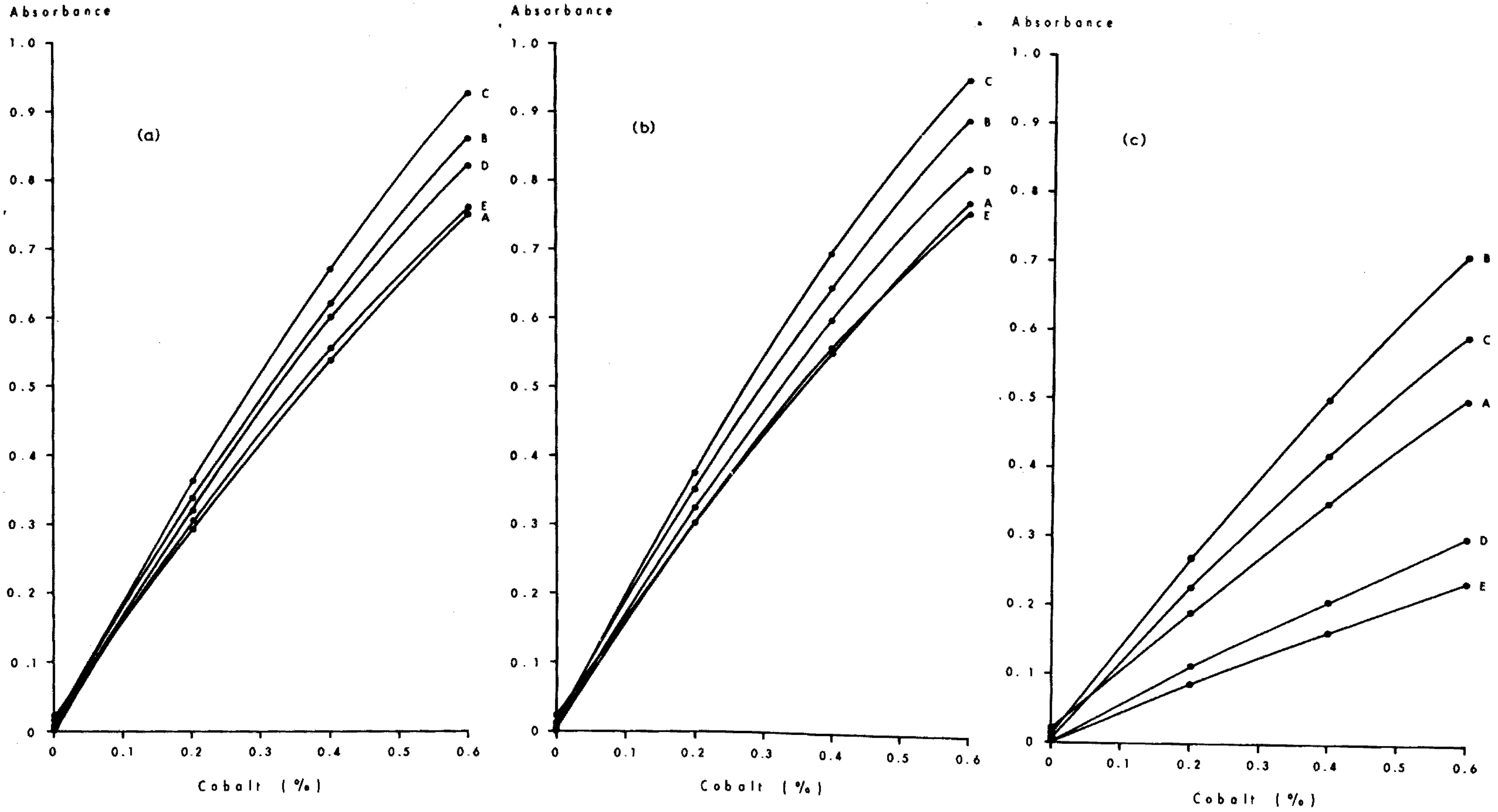

Fig. 1. The effect of flame type (Table I) on calibration curves in three acid media: (a) HCl (10%); (b) $HClO_4$ (10%); and (c) H_2SO_4/H_3PO_4 (3%/3%).

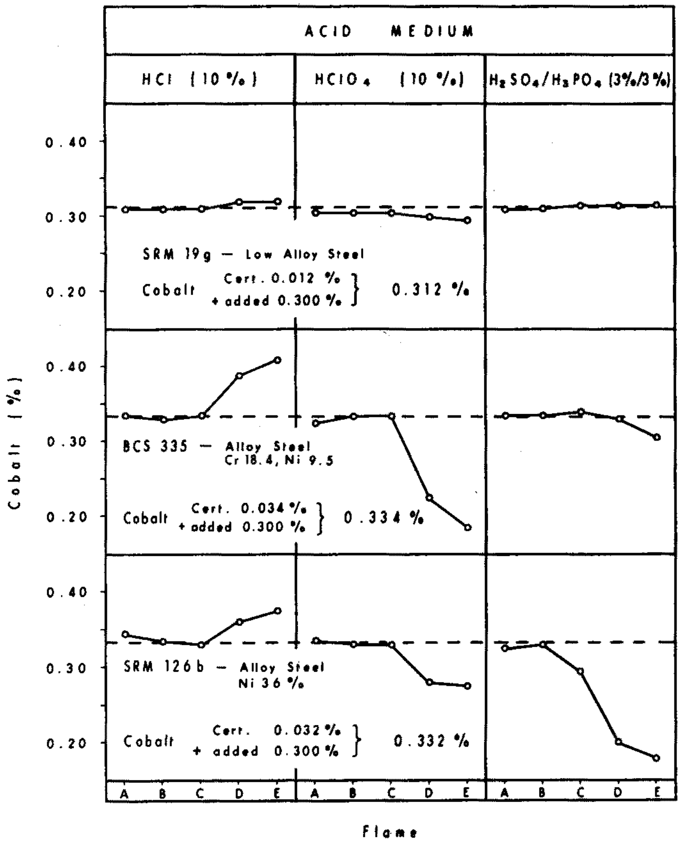

Fig. 2. The effect of flame type (Table I) on the accuracy of the determination of cobalt in three standard steels.

mechanism must be responsible for most of the background absorption and list molecular absorption, variation of the refractive index within the flame caused by vaporization of salt particles and continuous absorption caused by ionization of atoms, as possible causes. Of these, molecular absorption has been clearly identified in a number of instances[10-12].

An effective, if inconvenient, means of overcoming this type of interference is by close matching of the matrix elements of the assay solution in the calibration series.

The measurement of background absorption at a neighbouring non-absorbing line can also provide a useful means of compensation, if it is certain that background absorption is the same at both wavelengths. This need not be so, especially if the background absorption is caused by a molecular species.

Koirtyohann and Pickett[11] demonstrated how a continuum source could be used in overcoming background absorption. Because of the narrow width of the atomic absorption line, compared with the spectral band width of the monochromator, the atomic absorption component could be ignored when compared with the background absorption obtained with a hydrogen continuum as source. Thus by reading the atomic absorption, using a hollow-cathode lamp source, and subtracting the back-

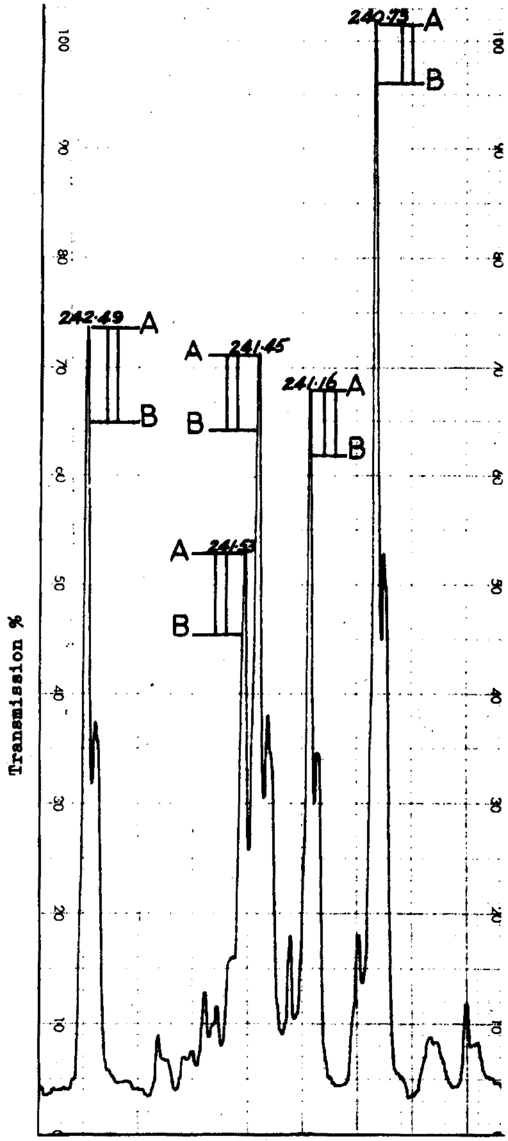

Fig. 3. The absorption effect of iron on the lines emitted by a cobalt hollow-cathode lamp in the region 243.0–240.0 nm. An absorption from level A to level B occurred when a solution of iron (1 g Fe/100 ml) was aspirated into an oxidizing air–acetylene flame.

ground absorption obtained using a hydrogen continuum source, a satisfactory correction could be applied. This method has been used subsequently by Fletcher[13] and Sandoz and Murray[14]. The disadvantages of the procedure are, firstly, the inconvenience of taking two readings and, secondly, the care needed in assuring that the atomization–flame system and the light path through the flame remain the same for both readings. Kahn[15] improved on the former technique by substituting the output from a deuterium arc for the reference beam of a double-beam atomic absorption spectrometer. By using a rotating sector mirror the light from the arc and from the lamp were passed alternately through the flame. In this way the background absorption was cancelled out. In this graphite crucible method, L'vov[16] employed a similar compensating system, using a hydrogen lamp to provide the continuum.

To obtain a better understanding of the nature and extent of the comparatively large absorption caused by iron and the smaller absorption caused by nickel the following investigation was carried out. The emission from a hydrogen lamp was scanned in the region 244.0 nm to 239.0 nm while solutions containing (A) perchloric

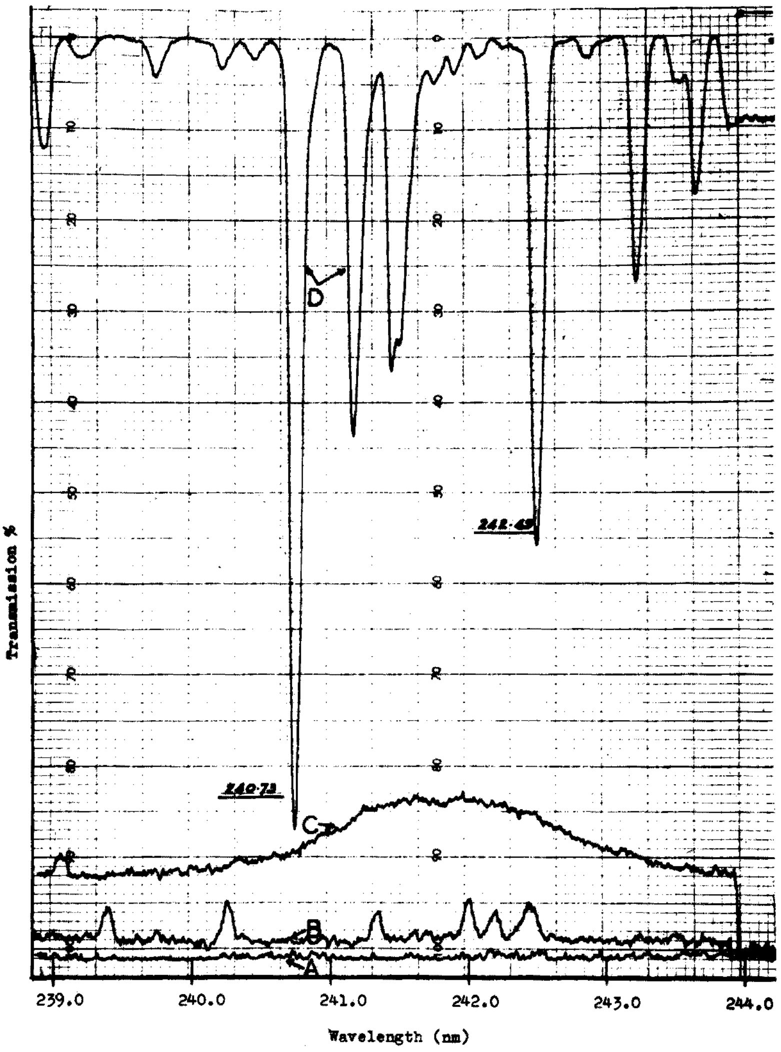

Fig. 4. The differing absorption effects of iron and nickel in the spectral range 244.0–239.0 nm. Solutions of iron and nickel were aspirated into an oxidizing air–acetylene flame while the emission from a hydrogen continuum was scanned over the range. (A) Aspirating 10% $HClO_4$; (B) aspirating nickel solution (1 g Ni/100 ml 10% $HClO_4$); (C) aspirating iron solution (1 g Fe/100 ml 10% $HClO_4$). A scan of the emission from a cobalt hollow-cathode lamp over the same range was also recorded (D).

acid (10 %), (B) pure iron in perchloric acid (10 %) and (C) pure nickel in perchloric acid (10 %) were aspirated into the flame. An oxidizing air–acetylene flame was used, and the scans were made sequentially on the same recorder paper. In order to locate the approximate positions of the cobalt lines in the region an additional scan (D) was made of the emission from a hollow-cathode lamp using the same slit width (25 μm). The result of this investigation is shown in Fig. 4. A broad absorption profile, apparently molecular in origin, caused by iron was shown to exist. The absorption profile of nickel, apart from a number of atomic lines, was much smaller.

The absorption caused by iron is strongly dependent on concentration (Fig. 5). Similar absorption profiles were obtained for hydrochloric, nitric, sulphuric and phosphoric acid solutions of pure iron and for aqueous solutions of the following iron salts: $FeNH_4(SO_4)_2 \cdot 12H_2O$, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $FeSO_4 \cdot 7H_2O$, which would indicate that the molecular compound responsible is formed in the flame.

The effect of flame type on the absorption profile of iron is shown in Fig. 6. As the flame becomes richer in acetylene and thus more reducing in nature the level of absorption diminishes and finally disappears. The likely cause of this absorption is the FeO molecule which would be expected to behave in this manner. This provides a satisfactory explanation for the variable blank readings obtained in Fig. 1. Also it is clear that other elements whose atomic absorption lines lie in the region of the absorption profile, *e.g.* gold at 242.8 nm, would be similarly affected.

Hermann and Alkemade[17] recorded the emission band spectrum of FeO obtained in an oxyhydrogen flame, showing the main peaks to be in the green and yellow regions of the spectrum. Their investigation did not cover the ultraviolet region. Absorption profiles caused by molecular species have been shown to follow closely the corresponding emission profiles[10,12]. An emission scan in the region of the observed absorption profile was recorded while an iron solution was aspirated into an oxidizing air–acetylene flame. The emission profile (dotted profile, Fig. 5) approximately follows the corresponding absorption profile.

NITROUS OXIDE–ACETYLENE FLAME

In their work on the determination of barium. Capacho-Delgado and Sprague[10] found that an interfering CaOH band, evident in the air–acetylene flame was almost completely eliminated by using a nitrous oxide–acetylene flame.

It was decided to investigate the use of the nitrous oxide–acetylene flame in this application as a possible means of overcoming the interferences encountered. A previous investigation into the use of this flame for the determination of cobalt in alumina was made by Fleet *et al.*[18]. They found the flame to be less sensitive than air–acetylene for the determination of cobalt but useful to a limited extent in dissociating alumina clotlets.

Chemical interferences encountered in the air–acetylene flame were found to be almost completely eliminated in the nitrous oxide–acetylene flame. The presence of 1 g/100 ml of iron, nickel or chromium had only minor effects (< 2 %) on the absorption obtained on a cobalt solution (20 μg ml^{-1} in 10 % $HClO_4$). Variations in the fuel-to-oxidant ratio were not as critical and variations in sensitivity with different acid media (Fig. 1) were absent. When identical scans to those used in Fig. 4 were repeated

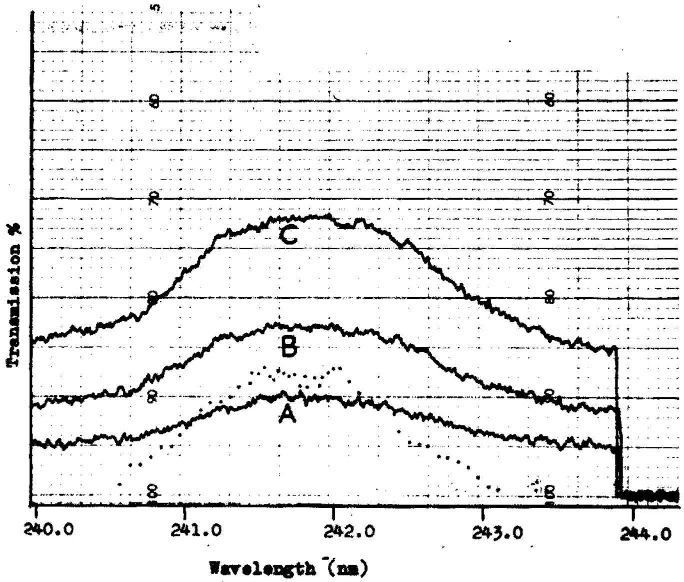

Fig. 5. Absorption profiles obtained by aspirating solutions of iron of varying concentration into an oxidizing air–acetylene flame while the emission from a hydrogen continuum was scanned over the spectral range 244.0–239.0 nm.
Solution: (A) 0.5 g Fe in 100 ml 10% $HClO_4$, (B) 1.0 g Fe in 100 ml 10% $HClO_4$, (C) 2.0 g Fe in 100 ml 10% $HClO_4$. The superimposed, dotted profile shows the emission recorded over the same range when an iron solution (1.0 g Fe/100 ml) was aspirated into the flame.

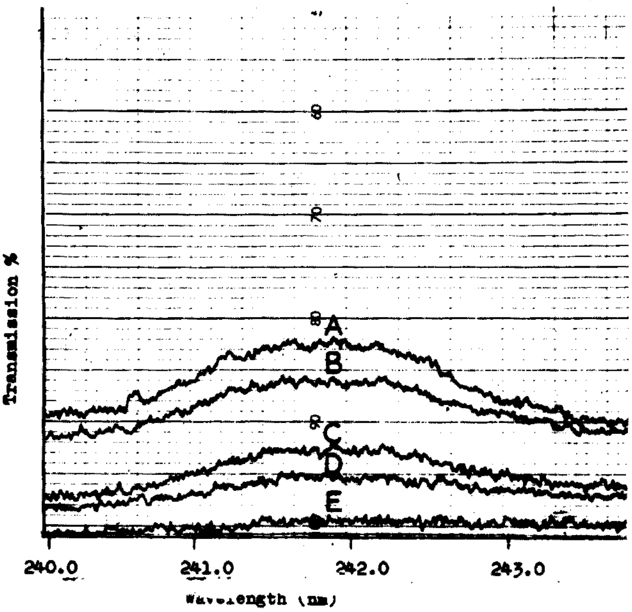

Fig. 6. The effect of flame composition on the observed absorption profile of iron (1 g Fe/100 ml). Gas settings on Varian Techtron AA5. In all cases the rotameter setting for air (20 p.s.i.) was 5.5. The rotameter settings for C_2H_2 (11 p.s.i.) were: (A) 2.2; (B) 2.5; (C) 2.8; (D) 3.0; (E) 3.5.

with the nitrous oxide–acetylene flame, the profiles obtained for both iron and nickel were the same as the baseline except for the atomic lines of nickel.

The sensitivity obtained in the nitrous oxide–acetylene flame was lower by a factor of *ca.* 2.5 times that obtained in the air–acetylene flame with the same 5 cm burner. Because of the high ionization potential of cobalt (7.8 eV), the loss of sensitivity caused by ionization should be quite small. This was borne out by the fact that an addition of 1000 μg K ml^{-1} had no noticeable effect on cobalt absorption. Fleet *et al.*[18] attributed the loss in sensitivity to an adverse effect on the atomization of cobalt by the strongly reducing cyanogen zone of the flame. According to Koirtyohann and Pickett[19], however, the free atom fraction of cobalt atoms should be at least as high in the nitrous oxide–acetylene flame as in the air–acetylene flame. An explanation for the loss of sensitivity has been provided by Willis[20] who has shown that two factors, (*i*) a decrease in solution yield, and (*ii*) an increase in flame volume, tend to produce lower sensitivities in the nitrous oxide–acetylene flame.

Apart from the loss of sensitivity, the nitrous oxide–acetylene flame appeared, on every other consideration, more suitable for the determination of cobalt by a.a.s. An analytical programme was therefore drawn up to confirm this.

EXPERIMENTAL

Apparatus

A Varian Techtron AA5 Atomic Absorption Spectrometer was used with the following auxiliary equipment:

1. Flame emission accessory.
2. Simple scanning motor (2 r.p.m.) fitted to the wavelength selector of the monochromator.
3. Hydrogen arc lamp.
4. Honeywell recorder-Electronik 194.

The following instrument settings on the Varian Techtron AA5 unit were used for the results obtained in Table II:

Wavelength, 240.7 nm.

Slit width, 25 μm (SBW 0.08 nm). When small absorbances were read with scale expansion, a slit width of 100 μm (SBW 0.33 nm) was used.

Light path, the centre of the light beam was focussed 7 mm above the burner head.

Nitrous oxide, pressure 20 p.s.i., rotameter setting 5.5.

Acetylene, pressure 12 p.s.i., rotameter setting 7.5.

Flame, the above gas settings provided a flame with a 1-cm red interzonal region.

Reagents

All reagents used were of analytical-reagent grade unless otherwise stated. References to acids imply concentrated acids unless otherwise stated.

Standard cobalt solution (0.1 *mg ml*$^{-1}$). Dissolve 0.1 g of pure cobalt sponge (Johnson Matthey Pty. Ltd.) in hydrochloric acid, add 50 ml of perchloric acid and take to fumes. Cool, and dilute to 1 l with distilled water.

Iron background solution (25 *mg ml*$^{-1}$). Dissolve 12.5 g of Specpure iron sponge (Johnson Matthey Pty.Ltd.) in hydrochloric acid. Cool, oxidize cautiously by drop-

TABLE II

RESULTS OBTAINED ON A RANGE OF LOW-ALLOY AND ALLOY STEELS WITH THE NITROUS OXIDE–ACETYLENE FLAME

Standard		*Cobalt (%)*		*Relative error*
No.	*Type*	*Certificate value and range*	*A.a.s.*	
BCS 327	Low-alloy steel	0.006 (0.006)	0.006, 0.006	0
SRM 55e	High-purity iron	0.007 (0.005–0.008)	0.006, 0.006	−14
BCS 149/2	High-purity iron	0.012 (0.011–0.013)	0.012, 0.012	0
BCS 326	Low-alloy steel	0.023 (0.021–0.025)	0.023, 0.023	0
BCS 335	Ni 9.5, Cr 18.5, Mn 1.0, Ti 0.5	0.034 (0.032–0.035)	0.035, 0.035	+3
BCS 336	Ni 9.5, Cr 17.5, Mo 2.5	0.063 (0.061–0.065)	0.066, 0.066	+5
SRM 160a	Ni 14, Cr 19, Mo 2.8, Mn 1.6	0.071 (0.068–0.075)	0.078, 0.078	+10
SRM 126a	Ni 36	0.032 (0.027–0.044)	0.030, 0.031	−5
SRM 339	Ni 9, Cr 17	0.096 (0.093–0.100)	0.097, 0.097	+1
BCS 277	Low-alloy steel	0.125 (0.118–0.136)	0.123, 0.123	−2
BCS 220/1	Cr 5, Mo 5, W 7, V 2	0.13 (0.12–0.13)	0.125, 0.125	−2
BCS 328	Low-alloy steel	0.17 (0.16–0.18)	0.170, 0.170	0
BCS 220	Cr 4.5, Mo 5, W 7, V 1.5	0.67 (0.64–0.68)	0.650, 0.650	−3
BCS 241/1	Cr 5, Mo 5, W 19.5, V 1.5	5.67 (5.58–5.73)	5.40, 5.45	−4
SRM 153a	Mo 9, Cr 4, W 2, V 2	8.47 (8.41–8.53)	8.50, 8.50	0
BCS 481	Cr 3.5, W 14	0.21 (0.19–0.22)	0.217, 0.217	+3
BCS 482	Cr 4, W 18	0.24 (0.21–0.27)	0.260, 0.260	+8
BCS 483	Cr 3, W 11	1.94 (1.90–1.99)	1.935, 1.935	0
BCS 484	Cr 5, W 22, Mo 1	10.2 (10.10–10.39)	9.90, 10.00	−2
BCS 485	Cr 4, W 18, V 1	5.06 (5.01–5.11)	4.90, 4.90	−3

wise addition of nitric acid, add 125 ml of perchloric acid and take to fumes. Cool, and dilute to 500 ml with distilled water.

Procedure

Dissolve 1 g of sample in 20 ml of a (3+1+1) hydrochloric acid–nitric acid–water mixture with warming. If tungsten is present, use a prior digestion in 20 ml of hydrochloric acid. Add 10 ml of perchloric acid and take to fumes. Cool, add 50 ml of distilled water and warm to dissolve salts. Cool, transfer to a 100-ml volumetric flask, dilute to the mark with distilled water and mix well. Filter, if necessary, sufficient solution for the analysis.

For the range 0.001%–0.500% Co use the solution as prepared.

For the range 0.50%–5.00% Co, use a 10-fold dilution prepared by taking 10 ml of the prepared solution in a 100-ml volumetric flask, and diluting to the mark with distilled water.

For the range 5.00%–10.00% Co, use a 20-fold dilution prepared by taking 5 ml of the prepared solution in a 100-ml volumetric flask, and diluting to the mark with distilled water.

Aspirate the solution into the flame using the recommended parameters. Scale expansion may be needed for the range 0.001%–0.020% Co. Calculate the cobalt content of the iron or steel by the calibration series technique[21].

Calibration series

(A) To a series of 100-ml volumetric flasks add 0.0, 0.5, 1.0, 2.5, 5.0, 10.0, 20.0, 30.0, 40.0 and 50.0 ml of standard cobalt solution (0.1 mg ml^{-1}). Add 40 ml of iron background solution (25 mg ml^{-1}) to each flask and dilute to the mark with distilled water.

These standards are used for the 0–0.5% Co range and represent 0, 0.005, 0.010, 0.025, 0.050, 0.100, 0.200, 0.300, 0.400 and 0.500% Co, when compared with the prepared undiluted solution.

(B) To a series of 100-ml volumetric flasks add 2.5, 5.0, 10.0, 20.0, 30.0, 40.0 and 50.0 ml of standard cobalt solution (0.1 mg ml^{-1}) and dilute to the mark with distilled water.

These standards are used for the range 0.5–10.00% Co and represent 0.25, 0.50, 1.00, 2.00, 3.00, 4.00 and 5.00% Co when compared with the 10-fold dilution and 0.50, 1.00, 2.00, 4.00, 6.00, 8.00, and 10.00% Co when compared with the 20-fold dilution.

RESULTS AND DISCUSSION

A wide range of low- and high-alloy steels was analysed and the results (Table II) were generally in good agreement with certified values. Assuming the accuracy of the certified values, the average relative error, disregarding sign, was 3.25%.

Detection limit and sensitivity

When the instrument was used on scale expansion, a detection limit of 0.0005% Co was obtained. On normal scale a reading of 0.300 absorbance was obtained for 0.200% Co.

Choice of solvent

The use of perchloric acid in this procedure was decided upon after preliminary work with the air–acetylene flame (Fig. 1 and Table I). However, in the nitrous oxide–acetylene flame, owing to the freedom from interference, the choice of solvent is less critical.

Some elements, in particular tungsten, tend to hydrolyse under oxidizing conditions and it has been suggested[22,23] that the hydrolysed product may occlude other elements from solution. For this reason several steels containing tungsten (up to 22% W) were included in the analytical investigation (Table II). Although no serious loss of cobalt was evident a phosphoric–sulphuric acid medium might be preferable for steels containing tungsten.

The author would like to thank the management of The Broken Hill Proprietary Co.Ltd. for permission to publish this work. He is indebted to Dr. J. B. Willis and Prof. W. F. Pickering for some useful suggestions and wishes to thank Dr. Willis for drawing his attention to and supplying a copy of Reference 20.

SUMMARY

In the determination of cobalt in iron and steel in air–acetylene flames at least

two types of interference may occur. In reducing flames the free atom population of cobalt is affected by the presence of alloying elements which behave differently in different acid media. In oxidizing flames the formation of a molecular compound of iron, probably FeO, in the flame gives rise to a substantial background absorption. These interferences may be overcome by substituting a nitrous oxide–acetylene flame.

RÉSUMÉ

Lors du dosage spectrophotométrique par absorption atomique du cobalt dans le fer et dans l'acier, avec flammes air–acétylène, il peut se produire deux types d'interférences, soit dans la flamme réductrice (par les autres éléments d'alliage), soit dans la flamme oxydante (par formation de composés moléculaires du fer, vraisemblablement FeO). Ces interférences peuvent être évitées en utilisant une flamme oxyde nitreux–acétylène.

ZUSAMMENFASSUNG

Bei der Bestimmung von Kobalt in Eisen und Stahl in Luft–Acetylen-Flammen können mindestens zwei Arten von Störungen auftreten. In reduzierenden Flammen wird der Anteil der freien Atome von Kobalt durch die Gegenwart von Legierungselementen beeinflusst, die sich in verschiedenen Säuremedien unterschiedlich verhalten. In oxidierenden Flammen führt die Bildung einer molekularen Verbindung von Eisen, wahrscheinlich FeO, in der Flamme zu einer wesentlichen Untergrundabsorption. Diese Störungen können durch Verwendung einer Lachgas–Acetylen-Flamme vermieden werden.

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NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY TIN

CHEMICAL SEPARATIONS AND NUCLEAR INTERFERENCES*

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Activation analysis has not so often been used for the determination of trace constituents in tin. The literature contains methods for determinations of arsenic, antimony, copper, silver, mercury, gold, oxygen, tantalum and potassium[1-14].

Three different methods involving reactor neutron activation are presented here for determinations of trace constituents in tin. In method I, the tin activities are separated from the non-volatile elements by distillation from a sulfuric acid–hydrobromic acid medium. The distillation residue is measured with a Ge(Li) detector and at least thirteen elements can be determined[15]. For the determination of arsenic, selenium and antimony which distil together with tin, additional separations are carried out[16]. Methods II and III deal with the determination of indium and manganese by means of the short-lived isotopes ^{116m}In and ^{56}Mn[17]; method II is based on anion exchange in hydrofluoric acid, whereas method III is purely instrumental.

Nuclear data

Natural tin consists of ten stable nuclides. Neutron irradiation can give rise to many radioactive isotopes. Table I[18-20] shows the reactions that have been observed during this work. It is obvious that not only tin radioisotopes are formed, but also radioisotopes of cadmium, indium, antimony and tellurium. Especially the ^{115}Cd, ^{114m}In, ^{116m}In and ^{124}Sb activities have to be watched as the determination of the corresponding elements is performed by the measurement of the same isotopes.

OUTLINE OF METHODS

Method I

In method I which is based on the distillation of tin, samples of 0.1–1 g together with standards were irradiated for 1 week at a thermal neutron flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1}. After irradiation, each tin sample was etched in hot hydrochloric acid and dissolved in a mixture of sulfuric acid and nitric acid. The solution together with 10 mg of gold carrier was transferred to a distillation apparatus as described by Scherrer[21], and heated under a carbon dioxide stream to 220°; 48% hydrobromic acid was added dropwise the hot solution at such a rate that the temperature remained between 200 and 220°. The distillate was absorbed in 6 *M* hydrochloric acid.

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** Aspirant of the N.F.W.O.

TABLE I

NUCLEAR DATA OF ISOTOPES FORMED BY REACTOR IRRADIATION OF TIN

(n,γ) Reactions

Reaction	*Cross section (barn)*	*Half life*	*Decay mode*	*γ-Energy (MeV)*
^{112}Sn(n,γ)^{113m}Sn	0.3	20 min	IT, EC	IT 0.079
(n,γ)^{113}Sn	0.8	115 d	EC (to ^{113m}In), γ	0.2552
^{116}Sn(n,γ)^{117m}Sn	0.006	14 d	IT, γ	IT 0.159; γ 0.1584
^{120}Sn(n,γ)^{121}Sn	0.16	26.2 h	β$^-$	—
^{122}Sn(n, γ)^{123m}Sn	0.15	40.3 min	β$^-$, γ	0.1602
^{124}Sn(n, γ)^{125m}Sn	0.14	9.6 min	β$^-$ [to ^{125}Sb (β$^-$ to ^{125m}Te)], γ	0.3320
(n, γ)^{125}Sn	0.004	9.65 d	β$^-$ [to ^{125}Sb(β$^-$ to ^{125m}Te)], γ	1.07, 0.81, 0.91

Threshold reactions

Reaction	*Half life*	*Decay mode*	*γ-Energy (MeV)*
^{112}Sn(n,2n)^{111}Sn	35.1 min	EC and β$^+$ [to ^{111}In(EC to ^{111m}Cd)], γ	
^{114}Sn(n,p)^{114m_2}In	44 msec	IT	0.150
(n,p)^{114m_1}In	50.0 d	IT, EC, γ	IT 0.1902; γ 0.5582, 0.7251
^{116}Sn(n,p)^{116m_2}In	2.3 sec	IT	0.164
(n,p)^{116m_1}In	54.1 min	β$^-$, γ	0.4170, 1.0971, 1.2934
^{118}Sn(n,α)^{115}Cd	53.5 h	β$^-$ (to ^{115m}In), γ	0.4925, 0.5277

Second order reactions

$$^{112}\mathrm{Sn}(n,\gamma)^{113m}\mathrm{Sn} \xrightarrow{\mathrm{EC}} {}^{113}\mathrm{In}(n,\gamma)^{114m_1}\mathrm{In}$$

$$^{112}\mathrm{Sn}(n,\gamma)^{113m}\mathrm{Sn} \xrightarrow{\mathrm{EC}} {}^{113}\mathrm{Sn} \xrightarrow{\mathrm{EC}} {}^{113m}\mathrm{In} \xrightarrow{\mathrm{IT}} {}^{113}\mathrm{In}(n,\gamma)^{114m_1}\mathrm{In}$$

$$^{112}\mathrm{Sn}(n,\gamma)^{113}\mathrm{Sn} \xrightarrow{\mathrm{EC}} {}^{113m}\mathrm{In} \xrightarrow{\mathrm{IT}} {}^{113}\mathrm{In}(n,\gamma)^{114m_1}\mathrm{In}$$

$$^{120}\mathrm{Sn}(n,\gamma)^{121}\mathrm{Sn} \xrightarrow{\beta^-} {}^{121}\mathrm{Sb}(n,\gamma)^{122}\mathrm{Sb}$$

$$^{122}\mathrm{Sn}(n,\gamma)^{123m}\mathrm{Sn} \xrightarrow{\beta^-} {}^{123}\mathrm{Sb}(n,\gamma)^{124}\mathrm{Sb}$$

Together with tin, arsenic, antimony and selenium were quantitatively distilled, whereas non-volatile elements such as cobalt, silver, copper, indium, and cadmium remained in the distillation residue. From the distillate, arsenic and selenium were separated by a sulfide precipitation. The arsenic sulfide and the selenium were filtered off, and from the filtrate containing tin and antimony, antimony was separated by elemental deposition on iron powder. The arsenic sulfide precipitate, the antimony fraction and the distillation residue were measured with a Ge(Li) detector.

Figure 1 shows a spectrum of the distillation residue. In this spectrum the two main photopeaks are due to ^{111}In, which is formed from the tin matrix. It appears that the 412-keV peak of ^{198}Au is hindered by the sumpeak of ^{111}In. For that reason and also because gold partially distils, after the measurement of the distillation

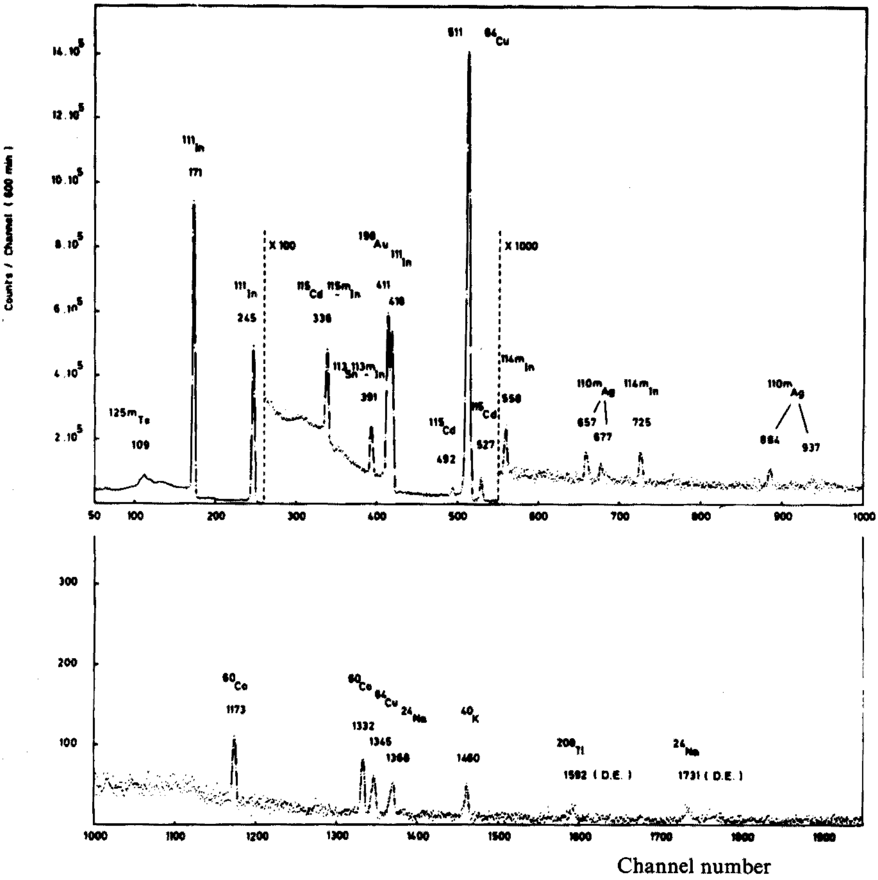

Fig. 1. Spectrum of the distillation residue measured with a Ge(Li) detector.

residue, a gold precipitation was carried out. In this way it was possible to correct for the loss of gold during the distillation, whereas measurement of the gold precipitate resulted in a purer ^{198}Au spectrum. To allow a better measurement of the long-lived non-volatile activities, the gold filtrate was measured after a 1-month decay time. A typical spectrum is shown in Fig. 2: ^{111}In has almost completely decayed.

The arsenic sulfide precipitate was also measured after a 1-month decay. This yielded a purer ^{75}Se spectrum.

The concentrations for the several elements were obtained from the total peak areas. For the calculation of the detection limits the criterion of Currie[22] was used. The results are given in Table II. For antimony the apparent antimony content formed from the second-order interference was calculated and subtracted. Correction of the ^{115}Cd activities for the ^{118}Sn(n,α)^{115}Cd contribution was done by simultaneous irradiation of tin samples with and without cadmium shielding. Finally correction of the indium concentrations for the ^{114}Sn(n,p)^{114m}In reaction and the second-order reactions was possible after determination of the exact indium content for samples 1 and 2. In this way the apparent indium content caused by the interferences was easily

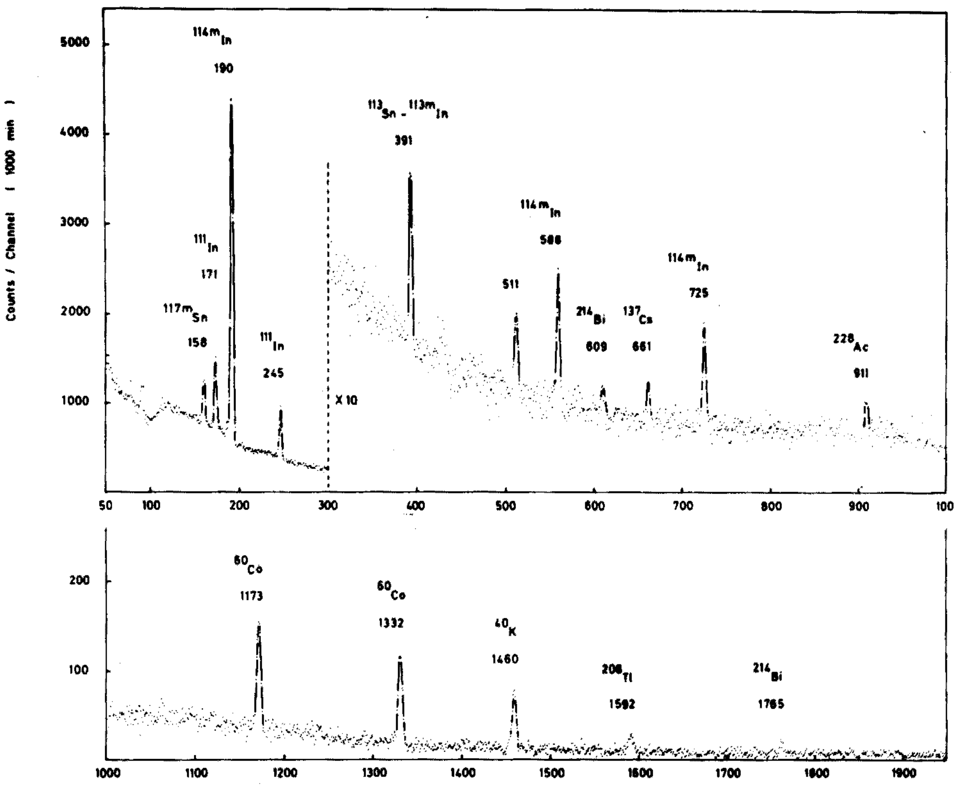

Fig. 2. Spectrum of the distillation residue after separation of gold.

obtained and this content was subtracted from the indium concentrations for samples 3 and 4. The true indium content of samples 1 and 2 was found by the methods II and III.

Method II

As has been mentioned, methods II and III deal with the determination of indium and manganese by measuring the ^{116m}In and ^{56}Mn activities. The determination of indium by means of ^{116m}In instead of ^{114m}In has three advantages: the determination is more sensitive, no second-order reaction is possible and the apparent indium content formed from ^{116}Sn(n,p)^{116m}In is about 130 times smaller[17] than that formed from ^{114}Sn(n,p)^{114m}In.

For method II, tin samples of 0.5 g were irradiated for 1 h at a thermal neutron flux of 10^{11} n cm^{-2} sec^{-1}. After irradiation each tin sample was etched in hydrochloric acid and dissolved in a mixture of hydrofluoric acid and hydrogen peroxide. The solution was transferred to the top of an equilibrated Dowex 1-X8 column and eluted under pressure at a rate of 0.1 ml sec^{-1}. After the solution had passed through, 5 *M* hydrofluoric acid was added to the column and eluted at the same rate. The eluate, which contained the indium and manganese activities, was measured with a NaI(Tl) well-type detector or a Ge(Li) detector.

TABLE II

ANALYSIS OF FOUR DIFFERENT TIN SAMPLES

Element	*Isotope used for the determination*	*γ-Radiations used (MeV)*	*Sample 1 (p.p.b.)*	*Sample 2 (p.p.b.)*	*Sample 3 (p.p.b.)*	*Sample 4 (p.p.b.)*
As	^{76}As	0.5592	47	230	11.9[a]	154[a]
Se	^{75}Se	0.1360, 0.2646	1.3	11	<6	220
Sb	^{124}Sb	1.6907	477	510	194	3.2[a]
Au	^{198}Au	0.4118	0.23	4	11	368
Cu	^{64}Cu	0.5110	—	—	39[a]	84[a]
Na	^{24}Na	1.3684	<0.3	3	<8	<50
Ga	^{72}Ga	0.8341	<0.4	<0.9	<13	<210
W	^{187}W	0.4793, 0.6857	<0.12	<0.16	<2.5	<20
Cd	^{115}Cd, ^{115m}In	0.3366, 0.5277	<5	<5	<10	1.1[a]
La	^{140}La	0.4868, 1.5954	<0.02	<0.03	<0.25	<1
Ag	^{110m}Ag	0.6578, 0.8845	14	11	<26	1.1[a]
Cr	^{51}Cr	0.3200	<2	<2	<13	<70
Fe	^{59}Fe	1.0986, 1.2915	<170	<170	<2[a]	36[a]
In	^{114m}In	0.1902	—	—	<20	660
Sc	^{46}Sc	0.8894, 1.1203	<0.02	<0.02	<0.2	<1
Ni	^{58}Co	0.8103	180	<100	<1.2[a]	19[a]
Zn	^{65}Zn	1.1154	<7	<7	<84	<600
Co	^{60}Co	1.1731, 1.3324	2.5	2.5	68	7.5[a]

[a] p.p.m.

TABLE III

DETERMINATION OF INDIUM AND MANGANESE AFTER SEPARATION FROM THE TIN ACTIVITIES: RESULTS

Sample	*In (p.p.b.)*		*Mn (p.p.b.)*	
	Measurement with NaI(Tl)	*Measurement with Ge(Li)*	*Measurement with NaI(Tl)*	*Measurement with Ge(Li)*
1	32.3	32.6	<5	<7
2	23.3 24.2[a]	22.8	<5	<12
5	44.3	42.7	<7	<11

[a] Irradiation with cadmium shielding.

The results are given in Table III. For sample 2 some irradiations were performed with cadmium shielding. From the difference between the concentration obtained in this manner and that obtained without cadmium shielding, the importance of the ^{116}Sn(n,p)^{116m}In threshold reaction and its interference in the indium determination could be obtained. It was found that the threshold reaction induced an apparent indium content of 0.4 p.p.b. without cadmium shielding. As this apparent content was only 2% of the indium concentration, it was neglected.

Method III

For method III no chemical separations were carried out. To distinguish the indium and manganese activities from the high tin activities a lead absorber was used. Tin samples of 2 g were irradiated for 1 h at a thermal neutron flux of 10^{11} n cm^{-2} sec^{-1}. After irradiation each sample was etched and dissolved in the same manner as for method II. The solution was measured with a Ge(Li) detector about 1 h after the end of the irradiation. Between the detector and the sample a lead absorber of 5 mm thickness was placed. In this way the 332-keV γ-radiation of ^{125m}Sn and especially the 160-keV γ-radiation of ^{123m}Sn were effectively absorbed. Further to inhibit back-scattering radiation in material close to the detector, the sample was surrounded with a lead cylinder of 3 mm thickness and to decrease the count rate caused by X-ray fluorescence in all this lead, a cadmium slab of 0.8 mm thickness was placed between the detector and the lead absorber.

The 160-keV peak was reduced to 0.01% of its original intensity, and the 332-keV peak to 18%, whereas the indium and manganese peaks at 1293.4 keV and 846.8 keV, respectively, used for the determination were only reduced to about 70%. The results are given in Table IV. The concentrations agree very well with those found by method II.

TABLE IV

INSTRUMENTAL ANALYSIS: RESULTS

Sample	*In (p.p.b.)*	*Mn (p.p.b.)*
1	33.7	<11
5	44.6	<13

DISCUSSION

For many elements, the concentrations do not exceed the detection limits, which are usually in the p.p.b. range. For method I, the sensitivity of the different elements strongly depends on the presence of other impurities. If ^{60}Co is the preponderant activity, which is the case for tin sample 4, the sensitivity for most elements decreases. Obviously this is due to the high Compton continuum. However, even in this case the detection limits are usually lower than 1 p.p.m.

The individual determinations, of which the given results are the mean values, were in good agreement for the tin samples 3, 4 and 5. The difference between the highest and the lowest value obtained was rarely more than 10%. For the tin samples 1 and 2, a greater concentration range was observed for the elements copper, silver, gold and cobalt. The concentrations for copper varied from 0.2 p.p.m. to 5.5 p.p.m. As this was due to surface contamination of the tin samples, no copper results are given.

SUMMARY

Eighteen trace elements were determined in high-purity tin by reactor neutron activation analysis. For the determination of 16 elements, a distillation from a sulfuric acid–hydrobromic acid medium was applied. Tin, arsenic, selenium and antimony were distilled, while the non-volatile elements remained in the distillation residue. After measurement of the distillation residue with a Ge(Li) detector, 13 elements were determined. For the determination of arsenic, selenium and antimony an additional separation from the tin activities was developed. Besides this distillation procedure, an anion-exchange method and an instrumental procedure were applied to determine indium and manganese in tin.

RÉSUMÉ

Dix-huit éléments, en traces, dans un étain très pur ont pu être dosés au moyen de l'analyse par activation neutronique. On utilise la distillation en milieu acide sulfurique–acide bromhydrique pour le dosage de 16 de ces éléments. Etain, arsenic, sélénium et antimoine sont distillés, alors que les éléments non-volatiles restent dans le résidu de distillation. Treize éléments sont dosés à l'aide d'un détecteur Ge(Li). On utilise un procédé avec échangeur d'anions pour déterminer indium et manganèse dans l'étain.

ZUSAMMENFASSUNG

Achtzehn Spurenelemente wurden in hochreinem Zinn durch Aktivierungsanalyse mit Reaktorneutronen bestimmt. Für die Bestimmung von 16 Elementen wurde eine Destillation aus einem Schwefelsäure–Bromwasserstoffsäure-Medium angewendet. Zinn, Arsen, Selen und Antimon wurden destilliert, während die nichtflüchtigen Elemente im Destillationsrückstand verblieben. Nach Messung des Destillationsrückstandes mit einem Ge(Li)-Detektor wurden 13 Elemente bestimmt. Für die Bestimmung von Arsen, Selen und Antimon wurde eine zusätzliche Abtrennung von den Zinn-Aktivitäten entwickelt. Neben diesem Destillationsverfahren wurden eine Anionenaustausch-Methode und ein instrumentelles Verfahren für die Bestimmung von Indium und Mangan in Zinn angewendet.

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THE DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN FERROMOLYBDENUM

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Molybdenum in ferromolybdenum has frequently been determined gravimetrically after precipitation as lead molybdate, but this method is tedious since a double precipitation of the molybdenum is required. Since ferromolybdenum consists mainly of molybdenum and iron with minor or trace amounts of carbon, silicon, phosphorus, sulphur, copper and perhaps other elements, it seemed possible that a differential spectrophotometric method could be developed for the determination of molybdenum in the alloy. For such a method it is desirable to use alloy samples with weights in the range 0.5–1 g, which corresponds to weights of molybdenum between 0.2 and 0.8 g; accordingly, the coloured compound used in the differential method must not have a high molar absorptivity. The simple compounds of the transition elements frequently have molar absorptivities between 1 and 200 and have been used in differential spectrophotometric methods. For example, Bastian[1] has used this technique to determine copper in copper-base alloys, and Bacon and Milner[2] have applied it to uranium in uranium metal and in triuranium octoxide.

Simple molybdenum(VI) compounds are generally colourless but simple molybdenum(V) compounds are coloured with low molar absorptivities and are readily produced from molybdenum(VI) on reaction with mild reducing agents.

A method for the differential spectrophotometric determination of molybdenum in solutions of ferromolybdenums after the reduction of molybdenum(VI) to molybdenum(V) and of iron(III) to almost colourless iron(II) is reported in this paper.

Preliminary investigations

Molybdenum(VI) in dilute hydrochloric acid is conveniently and quantitatively reduced to molybdenum(V) with an excess of hydrazine sulphate[3]. It was verified that molybdenum(VI) is, in fact, reduced to reddish-orange molybdenum(V) by hydrazine sulphate in 1.2 *M* hydrochloric acid on heating at 95° for 10 min. However, in this medium, iron(III) was not completely reduced to iron(II); a yellowish-green colour remained in a solution containing only iron after this treatment. When an excess of sodium sulphite solution was added to this yellowish-green solution, such that the hydrochloric acid concentration was *ca.* 0.13 *M*, and when the solution was heated to 95° for 10 min, the iron(III) was reduced to almost colourless iron(II). However, if this final hydrochloric acid concentration of *ca.* 0.13 *M* was exceeded, complete reduction of iron(III) to iron(II) did not appear to be achieved. Unfortunately, when this reduction treatment was applied to solutions of ferromolybdenums, a bluish-black colour was produced after adding hydrazine sulphate and heating (hydrochloric acid concentration 1.2 *M*). This colour was probably due to molybdenum blue or heteropoly blues formed in the dilute acid solutions; it should not be formed in more concentrated hydrochloric acid solutions but these were not compatible with complete reduction of iron(III).

Therefore, sulphuric acid media were examined. In sulphuric acid, molybdenum(VI) and iron(III) are reduced to molybdenum(V) and iron(II), respectively, by heating at 95° first with an excess of hydrazine sulphate and then with an excess of sodium sulphite. At the molybdenum reduction stage, the concentration of sulphuric acid in the solution was *ca.* 2.3 *M* and at the iron reduction stage, *ca.* 1.2 *M*. The final solution was reddish-orange in colour. Samples of ferromolybdenums reacted in a similar way to give clear reddish-orange solutions. These solutions showed a broad peak in the absorption spectrum with a maximum at 390 nm.

EXPERIMENTAL

Apparatus

A Hilger and Watts Uvispek Spectrophotometer was used for the differential spectrophotometry with accurately matched quartz cells of 1 cm light path.

Teflon beakers (150 ml) and covers (XIon Products, London) were used. Grade A volumetric glassware was used.

Reagents

Molybdenum sheet, either high-purity (Murex) or 99.9% (Koch-Light), and iron powder ("Specpure", Johnson and Matthey, London) were used. Nitric acid (d. 1.42), sulphuric acid (98% w/w) and hydrofluoric acid (40% w/w) were of analytical-reagent grade.

Copper sulphate solution (*6 mg Cu ml^{-1}*). Dissolve 2.358 g of A.R. copper sulphate pentahydrate in 100 ml of solution.

Orthophosphoric acid solution (*6 mg P ml^{-1}*). Dissolve 1.23 ml of A.R. orthophosphoric acid (d. 1.75) in 100 ml of solution.

Other stock solutions of metal ions for interfering effects were prepared from high purity metals or from salts of A.R. quality.

Procedure

To 0.6000 g of ferromolybdenum, accurately weighed, in a Teflon beaker add 5 ml of sulphuric acid (1+2). Carefully add in small portions, 3 ml of concentrated nitric acid, followed by 2 ml of concentrated hydrofluoric acid (Note 1). Heat the beaker on a hot plate at a low temperature and then increase the temperature gradually until white fumes of sulphur trioxide are evolved. Continue the fuming for a further 10 min. Cool the solution. A small yellow residue remains. Carefully add 15 ml of distilled water and then 4 ml of concentrated sulphuric acid gradually (Note 2). The precipitate usually dissolves, but if it does not, warm the beaker until a clear yellow solution is obtained. Add 20 ml of 3% (w/v) hydrazine sulphate solution and heat to *ca.* 95° for about 15 min. The reduction of molybdenum(VI) to molybdenum(V) occurs at this stage, and the solution gradually becomes reddish-orange. Cool the beaker and contents, add 20 ml of 1 *M* sodium sulphite solution and heat again at *ca.* 95° for about 20 min. The iron(III) is reduced to iron(II). Cool the solution, transfer it to a 100-ml graduated flask, and make up almost to the mark with distilled water.

At the same time, prepare in a similar way six standard solutions of molybdenum plus iron containing a total of exactly 0.6 g of these elements. The most dilute molybdenum solution should contain less molybdenum than that in the sample solution. If the most dilute molybdenum solution corresponds to $x\%$ molybdenum in a ferromolybdenum then the other solutions should correspond to $(x+2)\%$, $(x+4)\%$, $(x+6)\%$, $(x+8)\%$ and $(x+10)\%$ of molybdenum. The sample(s) for analysis should contain more than $x\%$ of molybdenum but less than $(x+10)\%$ of this element.

When all solutions have attained room temperature, make up to the mark with distilled water.

Select a wavelength of 390 nm. Add the most dilute standard molybdenum solution to one cell (Note 3) and a more concentrated molybdenum solution (a standard or a sample solution) to the other cell. Place the more dilute solution in the light path and set 0% transmission with the shutter in position. Remove the shutter and set 100% transmission by appropriate operation of the slit width and check controls. Place the other molybdenum solution in the light path and measure its absorbance. Repeat this procedure for all the standard and sample solutions (Note 4). Draw up a calibration graph for the standard solutions in the usual way and read off the concentration of molybdenum in the ferromolybdenum(s).

Note 1. Silicon should be removed as volatile silicon tetrafluoride. Otherwise a cloudiness due to silica is obtained in the final solution.

Note 2. When the solution is heated to fumes, only *ca.* 1 ml of sulphuric acid remains. It was found preferable in later work to add the 4 ml of concentrated sulphuric acid immediately after the hydrofluoric acid, before the fuming stage (see p. 218).

Note 3. The cells were cleaned by rinsing them in turn with acetone, benzene, concentrated sulphuric acid and finally distilled water. They were, of course rinsed with the appropriate solution before use.

Note 4. The absorbances of solutions measured differentially were constant for two days.

Tests for interfering elements

Phosphorus. Nine synthetic solutions were prepared each corresponding to 600-mg samples of ferromolybdenum containing 70% molybdenum, 30% iron, and 0, 0.03, 0.04, 0.05, 0.08, 0.10, 0.15, 0.20 and 0.25% of phosphorus. These solutions were analysed as described above. The absorbances of the molybdenum(V) solutions were measured against a standard solution containing 370 mg of molybdenum plus 230 mg of iron carried through a similar procedure. The percentage of molybdenum in each case was read from a calibration graph. Figure 1, curve A, shows the apparent molybdenum content of these 600-mg samples of simulated ferromolybdenums containing the different concentrations of phosphorus. There is no interference effect for 0.03% or less of phosphorus.

Copper. A similar graph is shown in Figure 1 (curve B) for simulated ferromolybdenums containing 70% of molybdenum and 0, 0.25, 0.5, 0.75 and 1.5% of copper. A black precipitate was also obtained in solutions containing copper at concentrations equivalent to or greater than 0.5% of copper in a ferromolybdenum.

Other elements. Similar studies were made with other elements. There were no interfering effects on the determination of molybdenum in simulated ferromolyb-

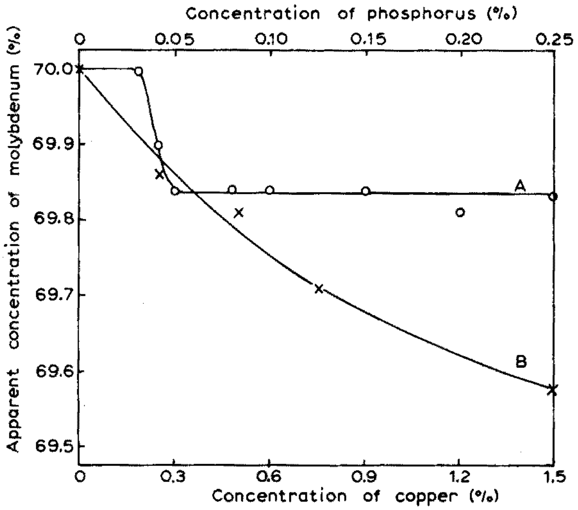

Fig. 1. The effect of low concentrations of phosphorus (curve A) and copper (curve B) on the differential spectrophotometric determination of molybdenum in simulated ferromolybdenums. All solutions contained the equivalent of 70.00% of molybdenum.

denums containing 70% of molybdenum, from 0.2% of arsenic, from 0.5% of lead, antimony, bismuth, tungsten, manganese, nickel and zinc, and from 3% of aluminium.

RESULTS FOR A SERIES OF FERROMOLYBDENUMS

The above method was applied to the analysis of fourteen ferromolybdenums; the results are shown in Table I (the first fourteen results).

Alloy No. 13 was analysed twelve times to establish the precision of the method. The average molybdenum content was found to be 75.32% with a standard deviation of 0.08% and a relative standard deviation of 0.11%.

When the investigation was nearing completion, it was realized that a slight improvement on the initial method was possible. In the initial method, on heating to fumes of sulphur trioxide, very little sulphuric acid remained in the beaker. Therefore it seemed better to add all of the sulphuric acid before fuming, for then *ca.* 5 ml of sulphuric acid was present in the beaker at the fuming stage (see Note 2). This slight amendment to the method would not affect the results for the first fourteen alloys in Table I. This was verified by analysing alloys Nos. 10 and 12 by the amended method. Results for the molybdenum contents of alloys 10 and 12 were 72.80% and 72.76%, and 75.20% and 75.26%, respectively. The average results of 72.78% and 75.23% are in close agreement with the values given for these alloys in Table I. Two further alloys (15 and 16) were analysed by the amended method and their molybdenum contents are also given in Table I.

DISCUSSION

The precision of the results obtained by the described method (Table I) is good but the average results are usually slightly low compared with the results given by the

TABLE I

RESULTS FOR THE DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN FERROMOLYBDENUMS

Alloy number	*Mo content* (%)[a]	*Mo content found* *Individual results* (%)	*Average* (%)	*Difference Col. 4 – Col. 2* (%)	*Corrected Mo content* (%)[b]	*Difference Col. 6 – Col. 2* (%)
1	46.5	46.30, 46.40, 46.41	46.37	−0.1	46.4	−0.1
2	48.6	48.33, 48.50, 48.41	48.41	−0.2	48.5	−0.1
3	60.9	60.95, 60.90, 61.05	60.97	+0.1	70.0	+0.1
4	68.9	69.00, 69.10, 68.75	68.95	+0.1	69.1	+0.2
5	70.03	69.91, 69.70, 69.93	69.85	−0.2	70.0	0
6	70.5	70.23, 70.33	70.28	−0.2	70.3	−0.2
7	71.41	71.33, 71.30	71.32	−0.1	71.4	0
8	71.9	71.79, 71.79	71.79	−0.1	71.9	0
9	72.46	72.40, 72.25, 72.45	72.37	−0.1	72.5	0
10	72.9	72.70, 72.75	72.73	−0.2	72.8	−0.1
11	72.98	72.88, 72.86	72.87	−0.1	73.0	0
12	75.3	75.10, 75.20	75.15	−0.2	75.3	0
13	75.40	75.35, 75.30, 75.41	75.35	0	75.5	+0.1
BCS 231/4	70.0	69.50, 69.60	69.55	−0.4	69.8	−0.2
15	69.10	68.67, 68.69	68.68	−0.4	68.9	−0.2
16	71.00	70.69, 70.85	70.77	−0.2	70.8	−0.2

[a] Determined by the supplier.

[b] See p. 218.

supplier. Ferromolybdenum seldom contains more than 0.05% of phosphorus and this could account for no more than 0.2% of the negative bias (see Fig. 1, curve A). However, the molybdenum content for BCS 231/4 determined by the described method was 0.4% low and it was interesting that a black precipitate was formed in the alloy solution on heating after the addition of sodium sulphite solution. Spectrographic analysis of the precipitate showed that it contained copper, and wet chemical analysis that it also contained sulphide. As reported earlier, a similar precipitate was obtained for simulated ferromolybdenums containing more than 0.5% of copper. Therefore, it seemed likely that at least part of the negative bias might be due to the alloy samples containing copper.

TABLE II

RESULTS FOR THE DETERMINATION OF COPPER IN FERROMOLYBDENUMS

Alloy	1	2	3	4	5	6	7	8
Copper content (%)	0.07	0.26	0.06	0.18	0.14	0.05	0.22	0.19
Alloy	9	10	11	12	13	BCS 231/4	15	16
Copper content (%)	0.22	0.14	0.27	0.11	0.22	0.55	0.53	0.10

The ferromolybdenums were analysed for copper content by conventional atomic absorption spectroscopy, with the results shown in Table II.

Corrections could be applied to the molybdenum figures in Table I for the copper contents of these alloys based on Fig. 1, curve B. When this was done the corrected results shown in Table I were obtained. The average negative bias was then −0.04%, which could be explained by the presence of trace amounts of phosphorus in these alloys. The results are considered to be good.

A satisfactory method has, therefore, been developed for the differential spectrophotometric determination of molybdenum in ferromolybdenums of low copper and phosphorus content. If a reducing agent other than sulphite can be found for the reduction of iron (III), the slight interference from copper should be eliminated. It is felt that sulphur dioxide and hydrazinium ions must have reacted to produce a little hydrogen sulphide which brought about precipitation of a small amount of copper sulphide. This precipitate could carry down small amounts of molybdenum and result in a slight lowering in the absorbance of the solution containing molybdenum (V).

We are indebted to High Speed Steel Alloys Ltd., London and Scandinavian Metallurgical Co. Ltd., Minworth Metals Ltd. and Murex Ltd. for supplying analysed samples of ferromolybdenum and to Murex Ltd. for a gift of high-purity molybdenum sheet.

SUMMARY

A differential spectrophotometric method is described for the determination of molybdenum in ferromolybdenums based on the reddish-orange molybdenum (V) species formed in sulphuric acid solution on reduction with hydrazine sulphate. Interference from iron is eliminated by reduction of the iron (III) to iron (II) with sulphur dioxide. Of the elements that could be found in minor or trace amounts in ferromolybdenum, only copper and phosphorus show slight interfering effects. When account was taken of the slight interference from copper in the determination of molybdenum in sixteen ferromolybdenums, results of good accuracy and precision were obtained.

RÉSUMÉ

On décrit une méthode spectrophotométrique différentielle pour le dosage du molybdène dans des ferromolybdènes, basée sur la formation de composés de molybdène(V) orange rouge, formés en milieu acide sulfurique par réduction à l'aide de sulfate d'hydrazine. L'interférence du fer est éliminée par réduction en fer (II) au moyen d'anhydride sulfureux. Parmi les éléments pouvant se trouver à l'état de traces dans un ferromolybdène, seuls le cuivre et le phosphore présentent une légère interférence.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Differentialmethode beschrieben für die Bestimmung von Molybdän in Ferromolybdän-Proben. Sie beruht auf der Bildung von rötlich-orangefarbenen Molybdän(V)-Spezies in schwefelsaurer Lösung nach Reduktion mit Hydrazinsulfat. Die Störung durch Eisen wird durch Reduktion von Eisen(III) zu Eisen(II) mit Schwefeldioxid beseitigt. Von den Elementen, die in

Ferromolybdän in geringen Mengen oder als Spuren vorkommen, stören nur Kupfer und Phosphor etwas. Durch Berücksichtigung der geringen Störung durch Kupfer bei der Bestimmung von Molybdän in sechzehn Ferromolybdän-Proben wurden Ergebnisse von guter Genauigkeit und Reproduzierbarkeit erhalten.

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SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN WITH DISODIUM *cis*-1,2-DICYANOETHYLENE DITHIOLATE

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Direct spectrophotometric techniques and neutron activation analysis are the most useful for the determination of traces of tungsten in ores and meteorites. The procedures require prior enrichment of tungsten by ion-exchange or liquid–liquid extraction processes. Atkins and Smales[1] have reported the use of activation analysis for the determination of tungsten in terrestrial materials. Tungsten is unusual in that its various ions do not readily react with many common nitrogen- and oxygen-containing ligands in acidic or alkaline media. In acidic medium tungsten has a strong tendency to form tungstic anhydride and in bases it forms the tungstates. Chan and Riley[2] investigated the coprecipitation of tungsten occurring in silicate rocks and natural waters and determined tungsten spectrophotometrically with toluene-3,4-dithiol. Liquid–liquid extraction of the tungsten complex with dithiol followed by photometric determination is probably the most widely used technique[3].

In the present paper a more selective method for the determination of tungsten is described. A rapid spectrophotometric method has been developed which is based on the stable red-violet complex formed by tungsten with disodium *cis*-1,2-dicyanoethylene dithiolate, commonly known as disodium maleonitrile dithiolate (MNT) which is soluble in aqueous 50% acetonitrile. The tungsten complex shows maximal absorbance at 570 nm and is stable in 1–3 *M* hydrochloric acid medium for several days. Very few cations and anions interfere in this determination. The complex which has a metal–reagent ratio of 1:4, obeys Beer's law from 1 to 20 p.p.m. with 2.7% relative analysis error per 1% absolute photometric error. The sensitivity of the colour reaction is 0.033 μg W cm^{-2}; the molar absorptivity of the complex is 5520.

EXPERIMENTAL

Apparatus and chemicals

Absorbances were measured with a Unicam SP600 spectrophotometer in 1-cm glass cells.

Acetonitrile. Acetonitrile (A.R., BDH) was stored overnight over phosphorus pentoxide, and then distilled.

Tungsten standards. Sodium tungstate (A.R., BDH) was dissolved in water and the tungsten content of the solution was determined gravimetrically by the 8-hydroxyquinoline method[4]. Weaker solutions of the metal ion were prepared by dilution as required.

Solutions of other diverse ions were prepared by dissolving analytical-grade chlorides, sulphates, or nitrates of the cations in water or dilute hydrochloric acid, and the sodium or potassium salts of the anions in water.

Twice-distilled water was used in all solution preparations.

Preparation of the reagent

The reagent, disodium-MNT, was synthesized by the procedure reported by Bähr and Schleitzer[5] with modifications suggested by Davison and Holm[6]. The procedure is outlined below.

Place finely powdered dry sodium cyanide (29.49 g) and 180 ml of pure dimethylformamide (DMF) in a 1-litre three-necked, standard-taper round-bottomed flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. Cool in an ice-water bath. Add carbon disulphide (36.2 ml) dropwise during 10 min, to form the red-brown cyanodithioformate. Then stir vigorously for 30 min, until a red-brown solid mass is produced. Stop the stirring, and add 500 ml of reagent-grade isobutanol; heat to dissolve the product. Filter the hot dark brown solution by suction using a filter aid to remove any residual sodium cyanide. Cool the filtrate in an ice-salt bath and agitate with a glass rod; the product crystallizes as a tan mass. Filter under suction and wash while still moist with anhydrous ethyl ether until the washings are pale yellow. Air-drying gives a yield of 160 g (71 %) of $NCCS_2Na \cdot 3HCON(CH_3)_2$. Dissolve this product in about 1400 ml of distilled water; after 24 h, sulphur is precipitated and the supernate is pale yellow. Filter off the sulphur and evaporate the filtrate to dryness in a rotary evaporator. Dissolve the yellow-brown solid in a minimal volume (about 600 ml) of boiling ethanol. Filter while hot to remove a small amount of insoluble material. Add anhydrous ethyl ether (250 ml) to the filtrate. The product separates on cooling in an ice-bath as pale yellow crystals. Collect the crystals under suction and wash with anhydrous ethyl ether until the washings are colourless. Dissolve in 450 ml of hot ethanol and filter. Addition of 200 ml of ethyl ether produces on cooling a pale yellow microcrystalline solid. Remove the last traces of alcohol by drying *in vacuo* (0.1 mm) at 80° for 24 h. Yield 27 g; m.p. 300° (decomp.). Analytical results: 25.5 % C, 0.04 % H, 14.75 % N, 34.3 % S; required for $Na_2C_4N_2S_2$: 25.8 % C, 0.0 % H, 15.05 % N, 34.45 % S.

A freshly prepared aqueous 0.2 % (w/v) solution of the reagent was used.

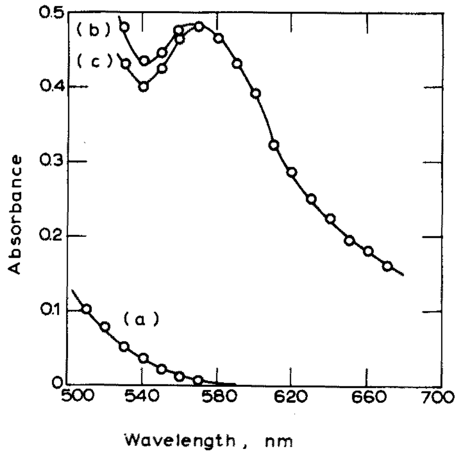
General procedure

Mix an aliquot portion of the standard tungsten solution, with 5 ml of the reagent solution and 4.2 ml of concentrated hydrochloric acid added in that order, and dilute with 12.5 ml of pure acetonitrile. Dilute to volume in a 25-ml flask with water. Prepare a reagent blank in exactly the same way. Mix thoroughly at room temperature, and measure the absorbance of the coloured complex at 570 nm in 1-cm cells.

RESULTS AND DISCUSSION

Absorbance curves

The absorbance spectra are shown in Fig. 1. The tungsten complex has maximal absorbance at 570 nm. The reagent exhibits negligible absorbance against a 50 % acetonitrile blank at that wavelength.



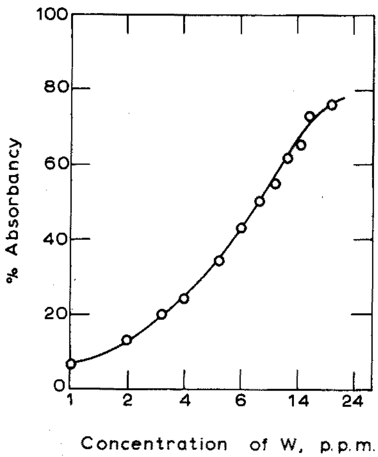


Fig. 1. Absorption curves. (a) Reagent blank against aqueous 50% acetonitrile, (b) metal complex against aqueous 50% acetonitrile, (c) 16 p.p.m. tungsten against reagent blank.

Fig. 2. Standard curve for the tungsten complex.

Choice of solvent

The reagent is soluble in water as well as in water-immiscible organic solvents such as chloroform, benzene, tributyl phosphate, isoamyl alcohol and other oxygenated solvents. The reagent in most of the organic solvents mentioned produces an intense colour which has appreciable absorbance at the wavelength of maximal absorbance of the coloured metal complex. The metal complex is not extractable into the water-immiscible solvents. The metal complex in aqueous solution becomes turbid within minutes. All these difficulties in measurement were overcome by using 50% aqueous–acetonitrile solvent media. The reagent has negligible absorbance at 570 nm and both the reagent and the complex are soluble in the solvent even when it is 3 *M* in acid, at which acidity the complex shows full colour development. The absorbance of the aqueous reagent solution remains constant for about 6 h after which it increases slowly. Accordingly, freshly prepared aqueous solutions of the reagent were always used and all solutions finally contained (1+1) water–acetonitrile solvent. When less than 45% acetonitrile was present, turbidity was not prevented.

Effect of variations of acid concentration, reagent and time

The colour of solutions containing 8 p.p.m. tungsten was developed as described above in the pH range 1–13, but no definite colour was formed. By varying the molar concentration of acid in the metal complex system, it was found that maximal colour development occurred at 1 *M* hydrochloric acid concentration; the absorbance remained constant from 1 *M* to 3 *M* acid at 570 nm. For all subsequent measurements, the acid concentration was adjusted to 2 *M* in the final volume.

A study of the reagent concentration with different quantities (1–10 ml) of reagent solutions added to 8 p.p.m. of tungsten indicated that 5 ml of 0.2% reagent was sufficient for full colour development.

The absorbance was measured at various time intervals. The complex showed constant absorbance even after 96 h.

Beer's law, optimal range and sensitivity

Test solutions with different concentrations of tungsten (1–24 p.p.m.) were prepared by the recommended procedure. A plot of absorbance values against tungsten concentration showed that the system obeyed Beer's law from 1 to 20 p.p.m.

The optimal concentration range for measurement was found by Ringbom's method[7]; the optimal range appeared to be 6–20 p.p.m. of tungsten (VI) (Fig. 2). The relative error per 1% absolute photometric error[8] for this range was 2.70%. The molar absorptivity was found to be 5520. The sensitivity of the colour reaction was 0.033 μg W cm^{-2}, according to Sandell's definition[3].

Effect of diverse ions

Table I summarizes the results of the interference study. A change of 0.005 in absorbance value was set as the tolerance limit for reproducible results. Fe(III), Cu(II), Co(II), Mn(II), Ni(II), V(V) produced colours at higher pH values, but could be tolerated upto the amount given in Table I at 2 *M* acid concentrations. Zn(II), Cd(II), Hg(II) and Bi(III) had no interference effect at 570 nm. Molybdenum(VI) seriously interfered by forming a coloured complex. Oxalate, citrate, tartrate, EDTA, phosphate and fluoride ions had no effect.

TABLE I

TOLERANCE FOR FOREIGN IONS
(Tungsten concentration: $1.087 \cdot 10^{-3}$ $M = 8$ p.p.m. Final volume: 25 ml)

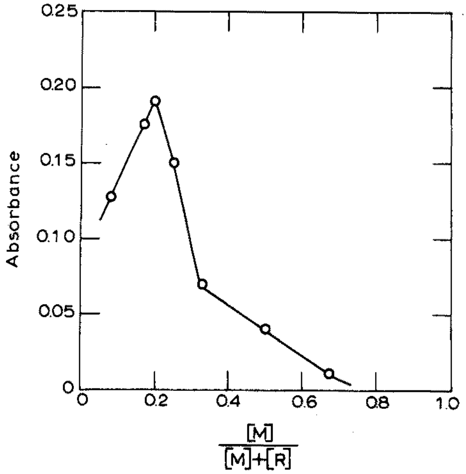
Ion	*Added as*	*Tolerance limit (p.p.m.)*	*Ion*	*Added as*	*Tolerance limit (p.p.m.)*
Ni(II)	$NiCl_2 \cdot 6H_2O$	8	Mo(VI)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	4
Pd(II)	$PdCl_2$	8	SO_4^{2-}	K_2SO_4	400
Pt(IV)	H_2PtCl_6	12	PO_4^{3-}	Na_2HPO_4	500
UO_2(II)	$UO_2(NO_3)_2 \cdot 6H_2O$	20	Oxalate	Oxalic acid	800
Cu(II)	$CuSO_4 \cdot 5H_2O$	20	Citrate	Citric acid	800
Co(II)	$CoCl_2 \cdot 6H_2O$	16	Tartrate	Tartaric acid	800
Fe(II)	$FeCl_3 \cdot 6H_2O$	8	EDTA	EDTA, di-Na salt	200
Cr(III)	$Cr_2(SO_4)_3$	30	F^-	NaF	200
V(V)	NH_4VO_3				

Composition of the complex

The composition of the tungsten complex was determined by the modified Job's method[9]. Equimolar solutions of the metal ion and reagent were mixed in complementary proportions to a total volume of 12 ml. After adjustment of acidity, the mixtures were diluted to 25 ml, so as to contain 50% acetonitrile. The plot of absorbance measured at 570 nm against mole fraction of metal is shown in Fig. 3; the formation of a 1:4 tungsten–MNT complex is indicated. The composition of the complex was verified by the mole ratio method of Yoe and Jones[10]. For a constant metal ion concentration, a plot of absorbance against increasing concentration of reagent (Fig. 4) gave a break at a metal–reagent ratio of 1:4.

Degree of dissociation and stability constant

The degree of dissociation and stability constant of the complex were calculat-



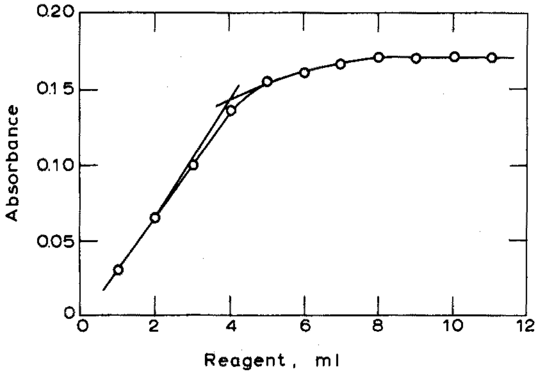


Fig. 3. Job's method of continuous variations. $[M] \equiv [R] \equiv 1.087 \cdot 10^{-3}$ *M*.

Fig. 4. Mole ratio plot. $[M] \equiv [R] \equiv 1.087 \cdot 10^{-3}$ *M*.

ed from Harvey and Manning's equation[11] and may be written as

$$K' = \frac{-\alpha C(n\alpha C)^n}{C(1-\alpha)}$$

where K' is the instability constant of the complex, C is the molar concentration of the complex and α is the degree of dissociation defined by $\alpha = (A_m - A_s)/A_m$, where A_m is the maximal absorbance obtained from the horizontal portion of the curve and A_s is the absorbance at the stoichiometric molar ratio of metal to reagent. The degree of dissociation of the complex and instability constant values were found to be 0.2059 and $4.267 \cdot 10^{-19}$. Hence the stability constant value is $2.344 \cdot 10^{18}$.

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SUMMARY

A new spectrophotometric method for determination of tungsten with disodium *cis*-1,2-dicyanoethylene dithiolate as reagent is described. Tungsten forms a red-violet complex in 50% water–acetonitrile solution and has an absorption maximum at 570 nm. The complex is stable in 1–3 *M* acid for several days. The colour reaction has a sensitivity of 0.033 μg W cm^{-2}. The tungsten complex obeys Beer's law over the range 1–20 p.p.m. with an optimal range of 6–20 p.p.m.; the molar absorptivity is 5520. The stability constant, K, of the complex was found to be $2.344 \cdot 10^{18}$.

RÉSUMÉ

Une nouvelle méthode spectrophotométrique est décrite pour le dosage du tungstène, au moyen de *cis*-1,2-dicyanoéthylènedithiolate disodique, comme réactif. Il y a formation d'un complexe violet rouge, en solution eau–acétonitrile (50 %) et maximum d'absorption à 570 nm. Ce complexe est stable plusieurs jours, en milieu acide 1–3 *M*. Sensibilité: 0.033 μg W cm^{-2} et coefficient d'extinction molaire: 5520. La coloration suit la loi de Beer de 1 à 20 p.p.m. (concentration optimale: 6–20 p.p.m.). La constante de stabilité *K* du complexe est de $2.344 \cdot 10^{18}$.

ZUSAMMENFASSUNG

Es wird eine neue spektrophotometrische Methode für die Bestimmung von Wolfram mit Dinatrium-*cis*-1,2-dicyanoäthylendithiolat als Reagenz beschrieben. Wolfram bildet in 50 %iger Wasser–Acetonitril-Lösung einen rotvioletten Komplex; das Absorptionsmaximum liegt bei 570 nm. Der Komplex ist in 1–3 *M* Säure einige Tage lang beständig. Die Farbreaktion hat eine Empfindlichkeit von 0.033 μg W cm^{-2}. Der Wolframkomplex gehorcht dem Beerschen Gesetz im Bereich 1–20 p.p.m.; der optimale Bereich ist 6–20 p.p.m.; der molare dekadische Extinktionskoeffizient beträgt 5520. Die Stabilitätskonstante, *K*, des Komplexes wurde zu $2.344 \cdot 10^{18}$ ermittelt.

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THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH PALLADIAZO

PART I. A STUDY OF THE PALLADIAZO–$Pd(H_2O)_4^{2+}$ SYSTEM

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In 1959, Popa *et al.*[1] tested 22 organic dyes in a search for specific analytico-functional groups for palladium(II). They found that, among others, the *o*-hydroxyazo group is specific under defined conditions for palladium(II). The number of such dyes that have since been tested is numerous, although few of the existing 500 *o*-hydroxymonoazo, 576 *o*-hydroxybisazo, and 195 *o*-hydroxytrisazo compounds listed in the Colour Index[2] have actually been tested for palladium. Instead, new *o*-hydroxyazo compounds have been synthesized; unless strong steric hindrance or inadequate medium conditions occurred, most of these compounds have shown a favourable reaction. All *o*-hydroxyazo compounds possess colour and absorb in aqueous solution in the visible spectrum. When they react with palladium(II), a bathochromic shift in the absorption maximum is generally produced, accompanied by a remarkable hyperchromic effect.

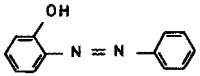
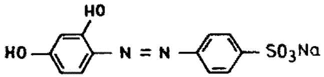
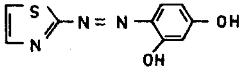
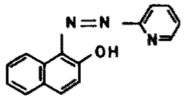
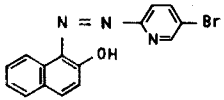
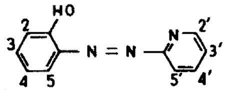
In 1955, Cheng and Bray[3] described 1-(2-pyridylazo)-2-naphthol as the indicator in titration of Zn(II), Cu(II) and Cd(II) with EDTA, and in the spectrophotometric determination of Zn(II), Cu(II) and Ni(II), including absorption spectra of the complexes formed with Fe(II), Pb(II), Co(II) and Pd(II). A spectrophotometric procedure for palladium(II) was not, however, developed[4] until 1958.

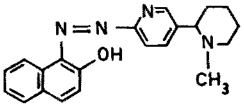
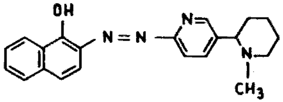
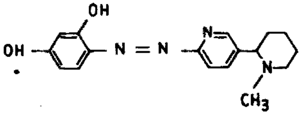
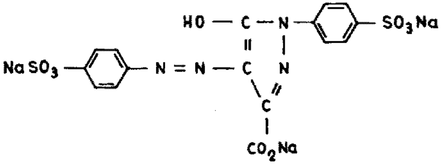
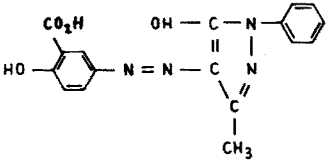
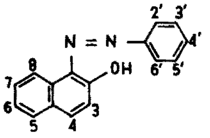
The main *o*-hydroxyazo compounds used recently for palladium(II) are summarized in Table I, with information on the characteristics of the complexes formed. Savvin *et al.*[32] have recently synthesized 12 new *o*-hydroxyazo compounds (chromotropic acid derivatives) and verified their favourable reactivity with palladium(II). The following general features can be seen from all these studies.

The complexes possess a high molar absorptivity, between $8.0 \cdot 10^3$ and $5.3 \cdot 10^4$ mmol^{-1} cm^2, which is only surpassed for palladium(II) by *p*-nitrosodimethylamine, *p*-nitrosodiethylamine[33] and *p*-nitrosodiphenylamine[34,35] but the ionic strength and the serious interferences caused by Cr(III), Co(II), Ni(II), $AuCl_4^-$, $RhCl_6^{2-}$, $PtCl_6^{2-}$ with the *p*-nitroso reagents is a disadvantage. With the *o*-hydroxyazo dyes, the complexes are usually of the ML_n type ($n=1$ or 2); the present study has proved the existence of an ML_3 complex which changes gradually to ML_2. All the complexes show maximal absorbance between 496 and 675 nm, despite their diverse molecular structures. The complexes are usually formed in media that vary from strongly acidic (6–8 N H_2SO_4) to neutral but rarely in alkaline medium; compound XXIX is an exception in this respect. It is reasonable to expect that *o*-hydroxyazo compounds

TABLE I

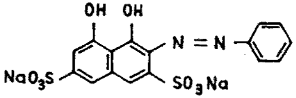
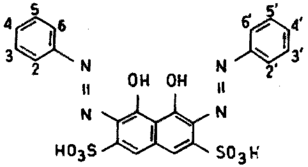
CORRELATION OF THE MAIN REACTION CHARACTERISTICS EXHIBITED BY DIFFERENT *o*-HYDROXYAZO-COMPOUNDS USED FOR THE DETERMINATION OF PALLADIUM(II)

No.	*Reagent formula*	*M. w.*	*pH*	$\lambda_{max.}$ *complex (nm)*	*Stoich.*	*S* ($\mu g\ cm^{-2}$)	ε ($mmol^{-1}\ cm^2$)	*Ref.*
I		198.22	4.5–6	546	ML_2	0.016	$8.0 \cdot 10^3$	5
II		262.22[a]	3–4	550	ML_2	0.085		6,7
III		211.24	2 *M* (H_2SO_4)	650	ML		$8.25 \cdot 10^3$ (isoam. OH)	8
IV		249.26	2.5	675	ML	0.006	$1.6 \cdot 10^4$	3, 4, 9–11
V		328.17	3	695	ML_2		$1.8 \cdot 10^4$	12
VI	 3-OH	215.20	6–8 *N* (H_2SO_4)	450 440	ML		$1.73 \cdot 10^4$ (isobut. OH) $1.85 \cdot 10^4$ (cyclohexanone)	13 14–16
VII	3-C_2H_5NH, 4-CH_3	246.30	0.1–0.7 *N* (H_2SO_4)	520	ML		$2.75 \cdot 10^4$	17
VIII	3-C_2H_5NH, 4-CH_3, 3′-Br	325.22	0.1–0.7 *N* (H_2SO_4)	530	ML		$4.04 \cdot 10^4$	17
IX	3-C_2H_5NH, 4-CH_3, 3′-5′-di-Br	404.13	0.1–0.7 *N* (H_2SO_4)	540	ML		$3.47 \cdot 10^4$	17
X	3-$(C_2H_5)_2$N	264.35	0.5–0.7 *N* (H_2SO_4)	560 ($CHCl_3$)	ML_2		$4.7 \cdot 10^4$	18

XI	3-$(C_2H_5)_2N$, 3'-Br	343.25	0.5–0.7 *N* (H_2SO_4)	575 $(CHCL_3)$	ML	$4.3 \cdot 10^4$	18
XII	3-$(C_2H_5)_2N$, 3'-5' di-Br	422.15	0.5–0.7 *N* (H_2SO_4)	590 $(CHCl_3)$	ML	$4.1 \cdot 10^4$	18
XIII		346.42	1.1	640	ML_2	$9.417 \cdot 10^3$ $(CHCl_3)$	19
XIV		346.42	2.5–2.7	660	ML_2	$1.288 \cdot 10^4$ $(CHCl_3)$	20
XV		311.35	3 5–7	600 520	ML_2	$1.06 \cdot 10^4$ $2.14 \cdot 10^4$	21
XVI		392.28	5.5	496			22
XVII		294.30	5.4	545			23
XVIII	 6,8-di-$NaSO_3$	408.4	6.5				24

(*Continued on p. 234*)

TABLE I (*continued*)

No.	*Reagent formula*	*M.w.*	*pH*	$\lambda_{max.}$ *complex (nm)*	*Stoich.*	*S* ($\mu g\,cm^{-2}$)	ε ($mmol^{-1}\,cm^2$)	*Ref.*
XIX	3,6-di-$NaSO_3$, 2′-CH_3	435.45[a]	5.4	610				23
XX	4′-$NaSO_3$	296.28	3–5.2	570	ML_2	0.026		25
XXI	3,6-di-$NaSO_3$, 2′-H_2AsO_3	519.21	2–10	520–80	ML	0.0106		25
XXII		392.34[a]	2.1–5.1	574	ML			26
XXIII	 4,4′-di-CH_3, 6,6′-di-HSO_3	716.42	0.0125–0.25 *N* ($HClO_4$, HCl)	620	ML		$4.0 \cdot 10^4$	27
			7	620			$4.31 \cdot 10^4$	28
XXIV	4,4′-di-Br, 6,6′-di-HSO_3	846.48	7.0	620			$3.00 \cdot 10^4$	28
XXV	4,4′-di-NO_2, 6,6′-di-HSO_3	779.27	6.8	595			$4.54 \cdot 10^4$	28
XXVI	6,6′-di-HSO_3	688.72	2.4	615			$3.95 \cdot 10^4$	28
XXVII	6-H_2AsO_3, 6′-HCO_2	696.46	7.0	620			$2.75 \cdot 10^4$	28
XXVIII	6,6′-di-H_2AsO_3	776.37	2.75	620	ML		$1.6 \cdot 10^4$	29
XXIX	4,4′-di-N $(C_2H_5)_2$		3.42	630	ML	0.007	$1.8 \cdot 10^4$ $\varepsilon_s = 1.26 \cdot 10^5$	30
			9.24	595	ML_2		$2.89 \cdot 10^4$	31
XXX	4,4′-di-H_2AsO_3	776.37	2.4±0.1	660	ML_3	0.0020	$5.3 \cdot 10^4$ $\varepsilon_s = 1.2 \cdot 10^6$	Present work
			2.4±0.1	660	ML_2	0.0050	$2.0 \cdot 10^4$ $\varepsilon_s = 3.31 \cdot 10^5$	

[a] In acid form.

of similar structure to XXIX, with substituents possessing $+M$ activating effects in a position *para* to the benzene nucleus, such as $-NR_2$, $-OR$, $-OH$, $-C(CH_3)_3$, etc., would also react with palladium(II) in alkaline medium.

EXPERIMENTAL

Reagents

Powdered palladium (Johnson and Matthey, London) was used to prepare standard solutions. Other chemicals used were of the highest available p.a. quality.

Instrumentation

A Beckman D.U. spectrophotometer, and a Perkin-Elmer 202 recording spectrophotometer, with Spectrosil 10-mm cells, were used.

Pye and Metrohm pH meters, and a Metrohm potentiograph model Combititrator 3D were used with various electrodes.

Preparation of palladium perchlorate

In order to avoid competitive complexing effects, palladium(II) was used in perchloric acid medium, where it exists[36] as $Pd(H_2O)_4^{2+}$.

Add 20 ml of aqua regia to accurately weighed 0.15–0.20 g samples of spectroscopically pure powdered palladium, and boil until dissolution is complete. Cool, add 15 ml of 70% perchloric acid and evaporate to near dryness. Allow to cool and add two 15-ml portions of the perchloric acid. After the last addition, evaporate to 20 ml and cool. Then dilute to 1 l with 0.5 M perchloric acid. The titre was checked with nioxime[37]. By dilution of this stock solution, other solutions with concentrations between 10.0 and 40.0 μg ml^{-1} were obtained.

The stability of $Pd(H_2O)_4^{2+}$ depends on its concentration, acidity, temperature and time of storage, and the relation between these variables is ill-established. In polythene containers, dark deposits of palladium metal appear after some time. Stock solutions in borosilicate flasks below 20° are stable for months. The diluted solutions are stable for only a few days; Sandell's observations should be considered[38].

Preparation of palladiazo solutions

Three batches of synthesized and purified 1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis[(azophenylene-*p*-arsonic)][39,40] were dissolved in water to give solutions ranging between $0.82 \cdot 10^{-3}$ and $1.15 \cdot 10^{-3}$ M. Elemental analyses for nitrogen and arsenic[41] as well as alkalimetric titrations showed the purity of the samples to be 95–100%. The three samples each showed a wide principal absorption maximum, between 530 and 550 nm, and two secondary maxima at 625 and 395 nm.

Optimal pH and wavelength determination for the palladiazo–Pd(II) complex system as a function of time

The absorbance of a spectrophotometric system at constant temperature in a given solvent is a function of pH, wavelength, time, ionic strength, and ligand : metal ratio. If the ionic strength is adjusted to < 0.1, and the ligand : metal molar ratio can be kept sufficiently high (10-fold) to avoid any intermediate stoicheiometry, the absorbance is a function of pH, λ and t only. To establish the optimal values of pH, wavelength and time, absorption spectra were recorded 5 min, 10 min, 2 h, 24 h, and 32 h after mixing $Pd(H_2O)_4^{2+}$ with the reagent; a blank solution of the same total ligand concentration and buffer was used. The pH of the solutions was carefully controlled by addition of perchloric acid, or perchloric acid–potassium hydrogenphthalate, or potassium hydrogenphthalate or sodium hydroxide in the acidic range; for pH 8.5–13, sodium hydrogencarbonate and/or sodium hydroxide were used. In all cases, the order of addition was: buffer, reagent (2.28 ml of $0.82 \cdot 10^{-3}$ M) and palladium (1.00 ml of 20.0 μg ml^{-1} solution in 0.1 M perchloric acid) in a 10-ml volumetric flask. The time

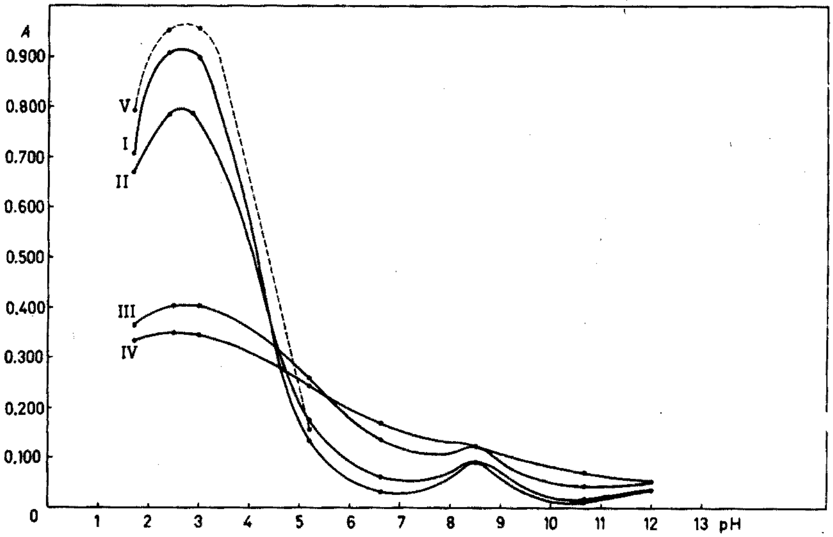


Fig. 1. Influence of pH and time on the formation of the palladiazo–Pd(II) complex compound. $\lambda = 670$ nm, $C_M = 1.87 \cdot 10^{-5}$ M, $C_L = 1.87 \cdot 10^{-4}$ M. (I) = 5 min; (II) = 10 min; (III) = 2 h; (IV) = 24 h; (V) = 5 min ($\lambda = 660$ nm). $l = 10.0$ mm. Measurements against reagent blank.

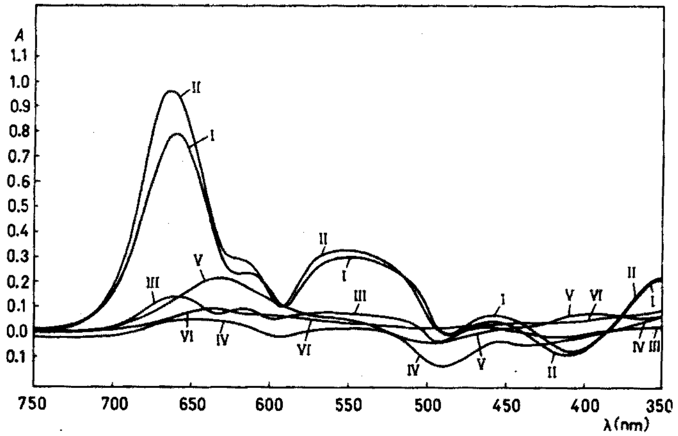


Fig. 2. Influence of pH on the formation of the palladiazo–Pd(II) complex species (recorded at optimal time of 5 min). $C_M = 1.87 \cdot 10^{-5}$ M; $C_L = 1.87 \cdot 10^{-4}$ M; $\mu = 0.08$. (I) pH = 1.7; (II) pH = 3.0; (III) pH = 5.2; (IV) pH = 6.6; (V) pH = 8.5; (VI) pH = 9.3. $l = 10.0$ mm. Measurements against reagent blank.

was measured from the addition of palladium(II), the solutions being mixed and diluted to the mark as quickly as possible. The spectrophotometer recording speed was 300 nm min^{-1}.

The effects of time and pH are shown in Figs. 1 and 2; from these studies, and from more detailed investigations[54] of the whole spectra between 350 and 750 nm at different times and pH values, the following conclusions were drawn.

1. In acidic media, maximal absorbance is obtained at 660 nm between 4 and 7 min; after 7 min, there is a rapid decrease in the absorbance, and constant absorbance (about 50% of the initial level) is not achieved until 3 h have elapsed. On passing from acidic to alkaline media (from pH 6.6 to 8.5), an hypsochromic effect is produced and another bathochromic effect appears with increasing alkalinity. In the initial period, the maxima are located at 635 nm (pH 8.5), 640 nm (pH 9.3–9.8) and 650 nm (pH 10.6–12). Between pH 4.3 and 5.6, the absorbance increases during the first 2 h and then decreases. From pH 5.6 to 12 there is an hyperchromic effect with time. Analytically speaking, the alkaline zone of pH is of no interest.
2. At least two complexes are formed depending on time.
3. No clearly defined isosbestic points are observed in the spectra obtained at 5 min (Fig. 2).
4. For maximal absorbance, the following conditions must be fulfilled: $\text{pH} = 2.4$, $\lambda = 660$ nm and $t = 5$ min.

KINETICS OF THE SYSTEM. ORDER AND REACTION VELOCITY

The evolution of the absorptivity was observed at pH 2.4 and $\lambda = 660$ nm as a function of time. For palladium(II) concentrations of $1.5 \cdot 10^{-5}$ and $0.75 \cdot 10^{-5}$ M, with 10-fold concentrations of reagent, an initial complex is formed between 30 sec and 4 min, and this complex exists between 4 and 7 min; subsequently, between 7 and 190 min, the complex is transformed to a more stable form, which remains essentially unchanged for at least 48 h. The existence of two molecular species seems probable. To determine the reaction order, Crowther and Kemp's treatment was applied[42,43]. If A_1 and A_2 are the concentrations of component A during times t_1 and t_2, respectively, the average value of $\mathrm{d}A/\mathrm{d}t$ is:

$$-\mathrm{d}A/\mathrm{d}t = A_2 - A_1/t_2 - t_1 \tag{1}$$

If the velocity reaction of an n-order equation is considered

$$-\mathrm{d}A/\mathrm{d}t = K_A A^n \tag{2}$$

then eqn. (1) can be expressed as:

$$\log(-\mathrm{d}A/\mathrm{d}t) = \log K_A + n \log A \tag{3}$$

The representation of $(-\mathrm{d}A/\mathrm{d}t)$ *vs.* $\log A$ should give a straight line, the slope n of which is the reaction order. As E_a, the absorbance value, is proportional to the concentration of palladium(II), it can be expressed as:

$$\log \frac{-\mathrm{d}E_a}{\mathrm{d}t} = \log \frac{E_{a1} - E_{a2}}{t_2 - t_1} \tag{4}$$

which is plotted as $\log \bar{E}_a = \log [(E_{a1} + E_{a2})/2]$ in Fig. 3. From these results, it can be

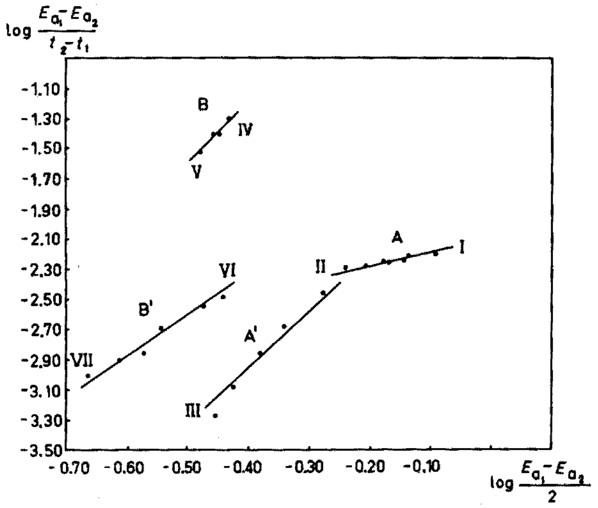


Fig. 3. Graphical evaluation of the kinetics exhibited by the palladiazo–Pd(II) system under maximal absorbance conditions. A and A′ refer to [Pd] $=1.5\cdot10^{-5}$ *M* and B and B′ to [Pd] $=0.75\cdot10^{-5}$ *M*. (I) 9–13 min; (II) 53–58 min; (III) 132–148 min; (IV) 30 sec; (V) 3 min; (VI) 27–30 min; (VII) 110–121 min. (A) $n=1$, (B) $n=4$, (A′) $n=3.3$, (B′) $n=3$.

concluded that the kinetic order of formation of the initial complex is 4; this is stable for 4–7 min. The equilibrium is displaced at 7–9 min (order 1); after 53–58 min, the kinetic order becomes 3 and after 180 min, an almost stable equilibrium is established. Thus two successive complexes are formed in the system, which are stable between 4 and 7 min and after 180 min, respectively. Between these time limits, both species must coexist, first one and then the other predominating.

In a system with two reacting species, the constant k of the reaction velocity is defined by:

$$-\mathrm{d}c/\mathrm{d}t = kc_{\mathrm{A}}^{n}c_{\mathrm{B}}^{m} \tag{5}$$

where c_{A} is the initial complex concentration, c_{B} is the hydrogen ion concentration, and n and m are the reaction orders referred to A and B respectively. Since c_{B} remains

$$-\mathrm{d}c/\mathrm{d}t = k'\,c_{\mathrm{A}}^{n} \tag{6}$$

integration yields:

$$(n-1)\,c_0^{n-1}k't = c_0/c_{\mathrm{A}}-1 \tag{7}$$

where c_0 is the initial value of c_{A} and the same concentration as palladium(II).

The absorbance of A is a linear function of the concentration of palladium(II); $c_0=E_0$ and $c_{\mathrm{A}}=E_{\mathrm{A}}$, and the absorbance of the initial complex is:

$$E_{\mathrm{A}} = E_0\,\frac{E_\infty - E_t}{E_\infty - E_0} \tag{8}$$

where E_0 is the absorbance for $t=0$, E_∞ the absorbance for complete reaction and E_t the absorbance at time t.

From eqns. (7) and (8),

$$(n-1)\,c_0^{n-1}\,k't = \frac{E_\infty - E_0}{E_\infty - E_t} - 1 \tag{9}$$

When the right-hand function is plotted against time, the result is a straight line with a slope $(n-1)\,c_0^{n-1}\,k'$.

The value of c_0 causes problems; although it is known for the initial kinetic period (30 sec to 3–4 min), it is not known for the final kinetic step of order 3. However, if the reaction is of order 1 (*cf.* Fig. 3), the initial concentration does not interfere in the calculation of the reaction velocity and from eqn. (3), the equation

$$k_A = \frac{E_{a1} - E_{a2}}{E_a(t_2 - t_1)}$$

can be deduced[42]. Then if the values between 9 and 53 min are used, it is possible to calculate a value for $k = 8.0 \cdot 10^{-3} \pm 0.4$ sec^{-1} at 23°.

STOICHEIOMETRY OF THE COMPLEXES

Conditions of constant ligand and variable cation concentrations

With fixed ligand and variable cation concentrations, the application of Yoe–Jones mole-ratio method[44] gave results which were rather difficult to interpret when a large excess of cation was present. When a more restricted range was used, the results shown in Fig. 4 were obtained. The existence of an initial ML_2 complex and a final ML complex can be easily observed. The importance of the time variable in stoicheiometry studies for this system is obvious.

When the spectra of two solutions with $C_M/C_L = 2$ and $C_M/C_L = 4.6$ were meas-

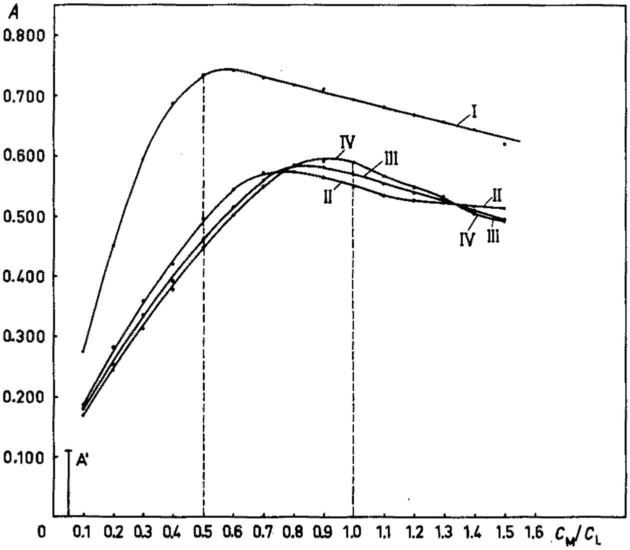


Fig. 4. Application of the mole-ratio method to the palladiazo–Pd(II) system (constant ligand concentration) as a function of time. $C_L = 4.6 \cdot 10^{-5}$ M, pH = 2.4, $\mu = 0.1$, $\lambda = 655$ nm. (I) 10 min; (II) 2 h; (III) 24 h; (IV) 96 h. A′ is the ligand absorbance.

ured at different time intervals, a kinetic isosbestic point was observed at 595 nm only for the metal:ligand ratio of 2. The isosbestic point is caused by an increase in the absorbance as a function of time in the 530–550 nm zone, which is the principal maximum of the reagent[54]. The initially formed complex releases a certain amount of ligand as a molecular species containing less ligand is formed. The reaction process (ignoring the water of hydration) can be expressed as:

$$Pd^{2+} + 2L \rightarrow PdL_2 \text{ (fast; 5–10 min)} \qquad [1]$$

$$PdL_2 \rightarrow PdL + L \text{ (slow; 15 min to 7–14 days)} \qquad [2]$$

$$Pd^{2+} + L \rightarrow PdL \text{ (fast)} \qquad [3]$$

Process [2] is facilitated by an increasing excess of palladium. For $C_M/C_L > 4.6$, no liberation of ligand is observed and the ML species is built directly:

$$PdL_2 + Pd^{2+} \rightarrow 2\,PdL \qquad [4]$$

Constant cation and variable ligand concentrations

With fixed cation and variable ligand concentrations, the mole-ratio method was again applied at different periods of time (Fig. 5). This Figure indicates the initial formation of a ML_3 complex which gradually changes to ML_2. As stated before, the

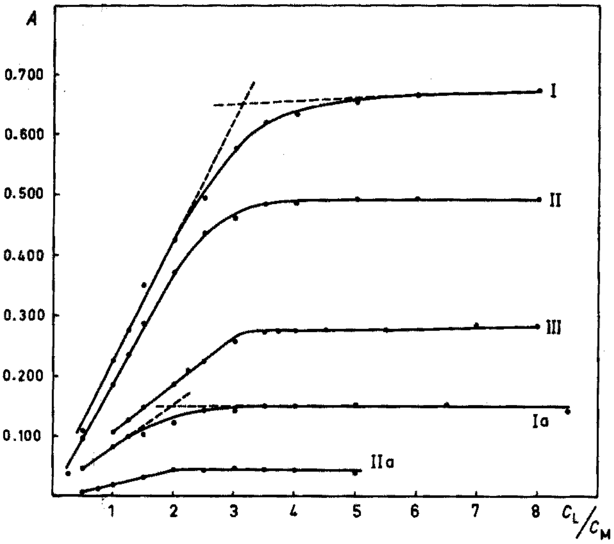


Fig. 5. Application of the mole-ratio method to the palladiazo–Pd(II) system (constant cation concentration).

	λ (nm)	t	μ	pH	C_M	Stoich.	ε (mmol⁻¹ cm²)	α	k	ε_S (mmol⁻¹ cm²)
I	660	5 min	0.08	2.4±0.1	$1.33\cdot10^{-5}$	ML_3	$4.9\cdot10^4$	0.10	$4.4\cdot10^{-17}$	$1.1\cdot10^6$
II	660	5 min	1.0	2.4±0.1	$1.33\cdot10^{-5}$	ML_3	$3.7\cdot10^4$	0.03	$5.3\cdot10^{-20}$	$8.25\cdot10^5$
III	660	10 min	1.0	0.5±0.1	$1.50\cdot10^{-5}$	ML_3	$1.8\cdot10^4$	0.05	$4.4\cdot10^{-18}$	$1.7\cdot10^5$
Ia	635	48 h	0.08	2.4±0.1	$1.33\cdot10^{-5}$	ML_2	$1.1\cdot10^4$	0.15	$2.8\cdot10^{-12}$	$5.2\cdot10^4$
IIa	635	24 h	1.0	2.4±0.1	$1.33\cdot10^{-5}$	ML_2	$0.3\cdot10^4$	—	—	

initial complex is stable between 4 and 7 min and the ML_2 complex between 2.5 and 48 h. The minimal C_L/C_M ratio needed to reach maximal absorbance is 7; above this value, the complex spectrum measured against a reagent blank (after 5 min) gives rise to a positive absorbance.

Some of the functions shown in Fig. 5 were obtained at higher ionic strengths ($NaClO_4$; curves II, III and IIa) in order to achieve better definition of stoicheiometry[45], although this procedure resulted in the production of secondary effects which caused a considerable reduction in the corresponding absorbance values. The correction of the free ligand concentration was done as discussed by Vosburgh and Cooper[46].

The degree of dissociation and the apparent instability constant were calculated as described by Harvey and Manning[45].

Considering the equilibrium as:

initial concentration $PdL_n \rightleftharpoons Pd^{2+} + nL,$

concentration in the equilibrium $c(1-\alpha) \quad \alpha c \quad n\alpha c$

where c is the total concentration of the undissociated complex in mol l^{-1}, we can write $K = [(\alpha c)(n\alpha c)^n]/[c(1-\alpha)]$. The n value for each complex has already been given and α is calculated by the relation $\alpha = (E_m - E_s)/E_m$, where E_m is the maximal absorbance obtained from the horizontal part of the curve, E_s the corresponding absorbance in the Yoe–Jones curve at the point of the theoretical molar stoicheiometry and c the total concentration of the complex and equal to that of palladium in the present case.

ε was calculated according to the A.C.S. definition[47] and ε_s as Sen Gupta[48] calculates the molar absorptivity through the sensitivity defined by Sandell[38]. The results are shown in the legend to Fig. 5.

Spectrophotometric evidence of the successive formation of the ML_3 and ML_2 species

Figure 6 shows the evolution of the absorbance spectra as a function of time

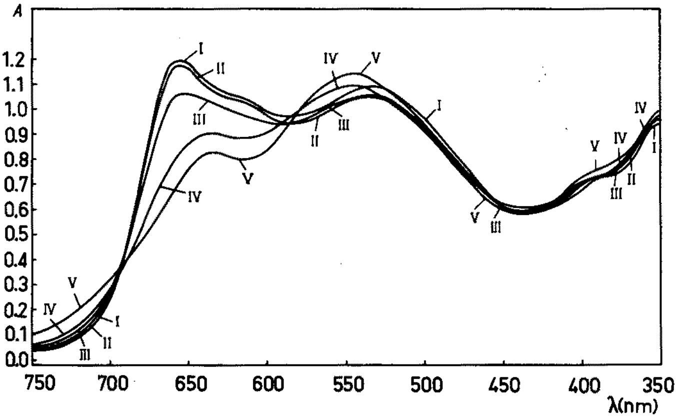


Fig. 6. Spectrophotometric evidence of the successive formation of two different complex species in the palladiazo–Pd(II) system under optimal conditions. Recording rate 300 nm min^{-1}. Spectra measured against a water blank. $C_M = 2.81 \cdot 10^{-5}$ M; $C_L = 5.65 \cdot 10^{-5}$ M; pH $= 2.4 \pm 0.1$; $\mu = 0.2$. (I) 3 min; (II) 6 min; (III) 15 min; (IV) 45 min; (V) 24 h.

when the ligand is in excess. As time elapses, the absorbance increases at 550 nm (maximal absorbance wavelength of the reagent), and decreases in the 660 nm region (maximal absorbance wavelength of the ML_3 complex), indicating liberation of the ligand from the newly formed complex.

The reaction process can be expressed under the conditions of excess of ligand (which is of practical analytical interest) as:

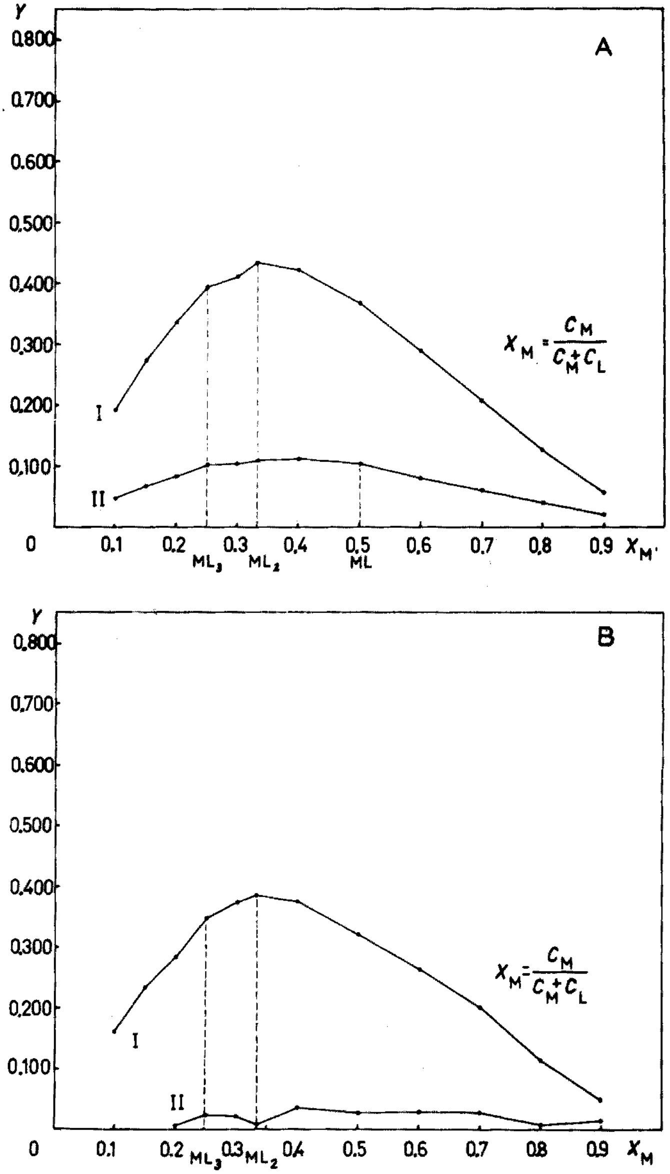


Fig. 7. Application of the isomolar variations method. $C_T = 4.0 \cdot 10^{-5}$ M; pH $= 2.4 \pm 0.2$. Spectra I measured at 660 nm after 5 min. Spectra II measured at 635 nm after 24 h. (A) $\mu = 0.08$, (B) $\mu = 0.10$.

$$Pd^{2+} + 3L \rightarrow PdL_3$$

between 30 sec and 4 min. This complex is stable between 4 and 7 min and then decomposes gradually:

$$PdL_3 \rightarrow PdL_2 + L$$

Application of the method of continuous variations

Job's procedure of continuous isomolar variations[49] was applied to the system; free ligand was corrected for as described by Vosburgh and Cooper[46]. The results obtained are shown in Fig. 7. Three different ionic strengths were used: 0.08, 1.0 and 3.0 ($NaClO_4$). A remarkable hypochromic effect was produced on Job's curve when the ionic strength was increased; the Job curves were completely deformed and under these conditions a blue precipitate was formed after 24 h.

At pH 2.4 and room temperature and with 0.1–1 *M* salt concentrations, $1.0 \cdot 10^{-3}$ *M* solutions of palladiazo are perfectly stable, but a precipitate is formed when dissolutions of about $4 \cdot 10^{-4}$ *M* in ionic strength 3 ($NaClO_4$) are attempted. This precipitate redissolves when the mixture is diluted with water or phthalate buffer at pH 2.4. The precipitation process is not instantaneous and similar effects were found with potassium nitrate. A solubility minimum was observed at ionic strength 3; the solubility increased with further increase in ionic strength.

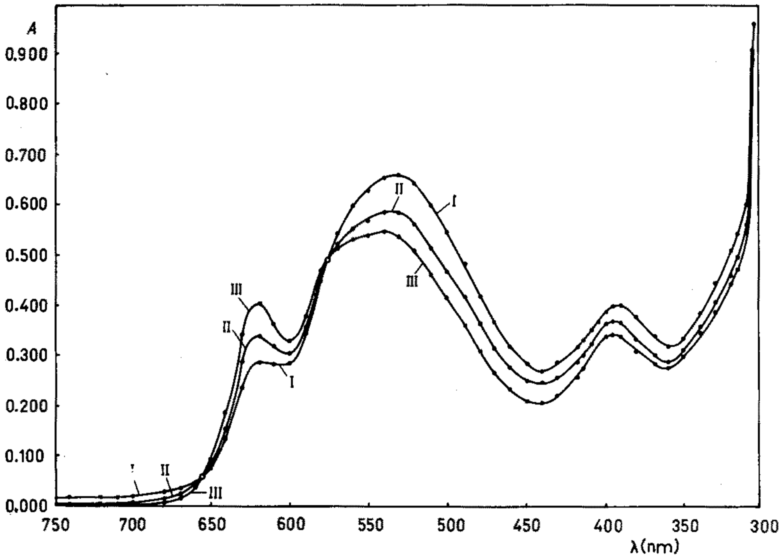


Fig. 8. Influence of ionic strength on the absorption spectra of the palladiazo reagent at pH 2.4. $c = 2.18 \cdot 10^{-5}$ *M*. (I) $\mu = 0.1$; (II) $\mu = 1.0$; (III) $\mu = 2.0$ ($NaClO_4$).

Figure 8 shows three spectra of the reagent at ionic strengths of 0.1, 1.0 and 2.0 at pH 2.4; spectra were recorded thirty days after preparation of the solutions. The appearance of two isosbestic points, a hypochromic effect over the principal maximum and a hyperchromic effect at the secondary absorption maxima can be observed.

Determination of the charge of the complexes formed

The charge of the ML, ML_2 and ML_3 species was determined by passing through ion-exchange resins, pure solutions of the complexes obtained by direct mixing of the components in suitable concentrations to obtain a pH comprised between 2 and 3, with an ionic strength lower than 0.1.

Small columns (1.5 cm diam.) were used to contain 7–12 cm beds of Dowex 1-X8, 50–100 mesh, or Dowex 50W-X8, 50–100 mesh; their exchange capacities were 14.8–25.4 and 23.4–40.0 meq, respectively. Both resins were washed with water leaving *ca.* 2 mm of water over the filter bed. To obtain the ML_3, ML_2 and ML complexes, $1.0 \cdot 10^{-3}$ *M* palladium(II) in 0.05 *M* perchloric acid and $1.0 \cdot 10^{-3}$ *M* palladiazo in

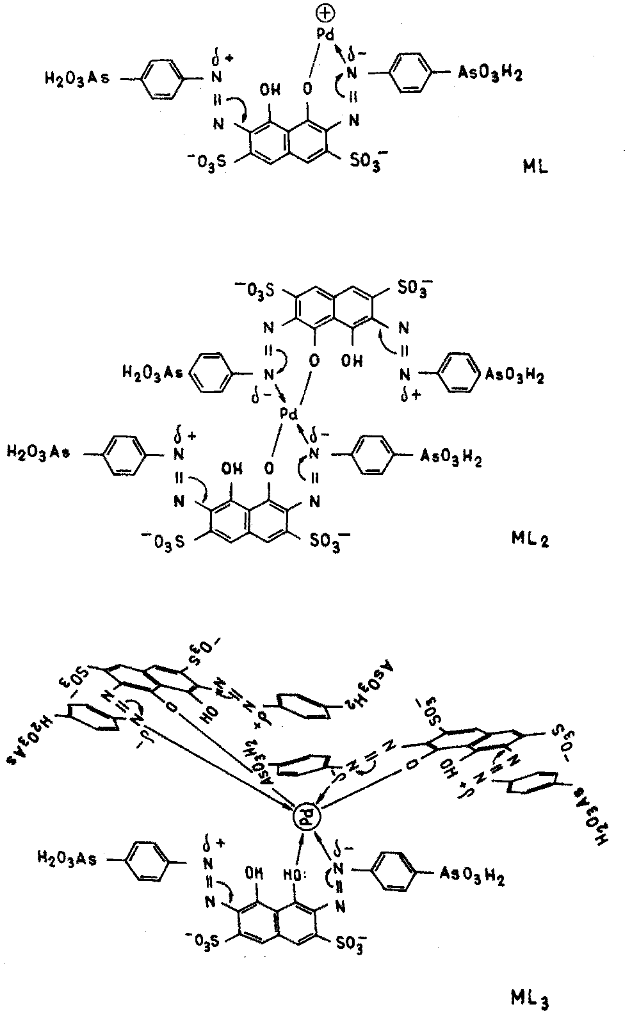


Fig. 9. Postulated reaction mechanisms implied in the formation of the three complex species.

free acid form dissolved in water, were used. The fixation process was followed easily, owing to the remarkable colour difference between the reagent and its complexes. The effluent rate was maintained at *ca.* 6 ml h^{-1} for the ML_2 and ML complexes, and *ca.* 12 ml h^{-1} for the ML_3 complex.

Palladiazo itself and the ML_3 and ML_2 complexes were quantitatively retained on Dowex 1 resin but not retained by Dowex 50 resin. In the case of the ML_3 complex percolated 3 min after its preparation, two fixation zones were observed. The ML complex was quantitatively retained by Dowex 50 but not retained by Dowex 1. It is clear therefore that palladiazo and the ML_3 and ML_2 complexes are anionic in nature whereas the ML complex is cationic[54].

Probable structures of the characterized complexes

The most probable formulae of the complexes formed are shown in Fig. 9 where the electron displacement brought about by $Pd(H_2O)_4^{2+}$ in the 1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis[(azophenylene-*p*-arsonic)] molecule is expressed by the conjugative mechanism indicated. Half of the molecule is deactivated by the mutual influence of the two azo-conjugated groups. In one of them, one N remains with a positive charge which rules out the formation of any additional complex with $Pd(H_2O)_4^{2+}$ other than those indicated of the ML_n-type ($n = 1, 2, 3$), provided that palladiazo is not placed in a medium so strongly acidic or alkaline as to cause any change in the molecule itself (*e.g.* quinone hydrazonic tautomery, protonation of azo groups, etc.[40]).

In the case of the complex formed by arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis[(azophenylene-*o*-arsonic)] with lanthanum(III), Savvin and Volynets[50] suggest the above-mentioned electron displacement and postulate the same conjugative mechanism, although the existence of an *o*-arsonic group in the arsenazo III reagent allows for additional possibilities of union of the reagent with the cation. Welcher[51] postulates the same general structure for the *o*-hydroxyazo complexes built by many organic reagents with cations. The actual spatial configuration of the complex remains unknown.

ANALYTICAL UTILIZATION OF THE COMPLEX

In the spectrophotometric determination of palladium with palladiazo, media with ionic strengths greater than 0.2–0.3 should be avoided, both in the spectrophotometric blank reagent reference solutions and in the samples. Because of the high sensitivity of the system, salt concentration is not an important problem; samples decomposed by normal methods so that palladium is accompanied by abundant sodium and potassium salts can be handled by making strong dilutions.

The Beer law is obeyed under the optimal conditions as shown in Fig. 10. The validity of Beer's law was also verified at 670 nm and pH 3.5, 7.0 and 9.20 for the palladium(II)–palladiazo system; the absorbances were about 8 times less at pH 7.0 and 9.20, than those obtained under the above optimal conditions. Nevertheless, the method could be useful for determination of palladium(II) in alkaline medium.

The Ringbom curves[52] were plotted from the data obtained. These and other analytical characteristics of the $Pd(H_2O)_4^{2+}$–1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis[(azophenylene-*p*-arsonic)] system are summarized in Table II.

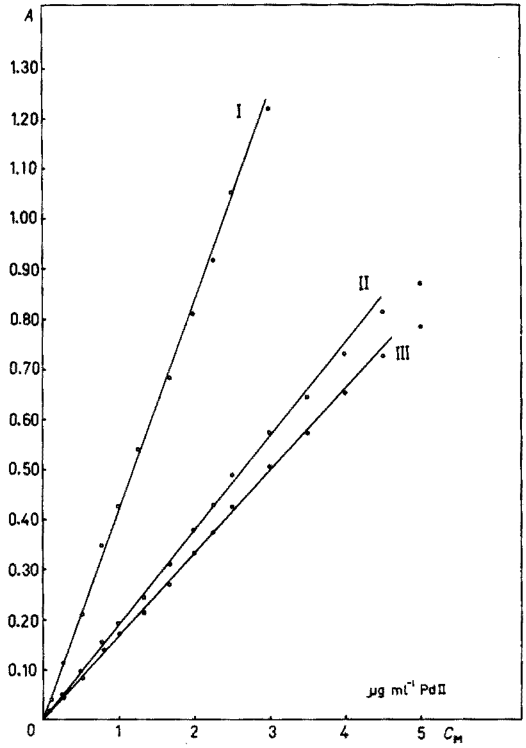


Fig. 10. Conformance of the ML_3 and ML_2 complexes to Beer's law under optimal conditions. $C_L = 1.5 \cdot 10^{-4}$ M, $pH = 2.4 \pm 0.1$, $\mu = 0.1$, $\lambda = 660$ nm. (I) 5 min; (II) 3 h; (III) 24 h.

TABLE II

MAIN ANALYTICAL CHARACTERISTICS OF THE $Pd(H_2O)_4^{2+}$–PALLADIAZO SYSTEM

λ	660 nm	660 nm	660 nm
pH	2.4 ± 0.1	2.4 ± 0.1	2.4 ± 0.1
Measuring time	5 min	3 h	24 h
Probable formula of complex[a]	$[Pd(C_{22}H_{14}N_4O_{14}S_2As_2)_3H]^{6-}$	$[Pd(C_{22}H_{14}N_4O_{14}S_2As_2)_2]^{4-}$	
Beer–Lambert range	0.1–2.5 μg ml^{-1}	0.1–4 μg ml^{-1}	0.1–4.5 μg ml^{-1}
Optimum concentration range (Ringbom[52])	0.4–2 μg ml^{-1}	0.7–4 μg ml^{-1}	0.7–4.5 μg ml^{-1}
% Relative analysis error per 1% T absolute photometric error (Ayres[53])	3.1	3.5	3.6
Sensitivity (Sandell[38])	0.0022 μg cm^{-2}	0.0053 μg cm^{-2}	0.0061 μg cm^{-2}

[a] Assuming the two sulphonic groups to be completely ionized.

SUMMARY

The reactions between the *o*-hydroxyazo reagent trivially named palladiazo and $Pd(H_2O)_4^{2+}$ are discussed and the optimal formation conditions for the complex are established. At pH 2.4 (in absence of chloride), a ML_3 complex is formed; after 7 min, this is transformed to a ML_2 species and ligand is liberated. The reaction based on the ML_3 complex has a Sandell sensitivity of 0.0020 μg cm^{-2}. In addition to the complex of major analytical interest, the ML_2 and ML species are also characterized; probable structures and mechanisms are given. The accuracy, precision, sensitivity and optimal concentration ranges for practical spectrophotometry with palladiazo are outlined.

RÉSUMÉ

On examine les réactions entre le réactif *o*-hydroxyazo (nommé palladiazo) et $Pd(H_2O)_4^{2+}$, et les conditions optimales de formation du complexe. Au pH 2.4 (en l'absence de chlorure) on obtient un complexe ML_3. On indique également précision, exactitude et sensibilité, ainsi que les concentrations optimales pour un dosage spectrophotométrique.

ZUSAMMENFASSUNG

Die Reaktionen zwischen dem *o*-Hydroxyazo-Reagenz Palladiazo und $Pd(H_2O)_4^{2+}$ werden diskutiert und die optimalen Bildungsbedingungen für den Komplex festgestellt. Bei pH 2.4 (in Abwesenheit von Chlorid) wird ein ML_3-Komplex gebildet; nach 7 min wandelt sich dieser unter Ligandabgabe in einen ML_2-Komplex um. Die zu dem ML_3-Komplex führende Reaktion hat eine Sandell-Empfindlichkeit von 0.0020 μg cm^{-2}. Ausser dem Komplex von grösstem analytischem Interesse werden auch die ML_2- und ML-Spezies charakterisiert; die wahrscheinlichen Strukturen und Mechanismen werden erörtert. Die Genauigkeit, Reproduzierbarkeit, Empfindlichkeit und die optimalen Konzentrationsbereiche für die praktische Spektrophotometrie mit Palladiazo werden angegeben.

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THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH PALLADIAZO

PART II. A STUDY OF INTERFERENCES AND THE DETERMINATION OF PALLADIUM IN CATALYSTS AND MINERALS

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In the previous paper[1], the palladiazo–$Pd(H_2O)_4^{2+}$ system has been discussed; palladiazo is the trivial name of 1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis(azophenylene-*p*-arsonic).

In this system two complexes, ML_2 and ML_3, are formed and their characteristics of analytical interest have been described[1]. In the present paper, some analytical applications of the palladiazo reagent are demonstrated. The method is shown to be not only sensitive for palladium but remarkably free from interferences.

EXPERIMENTAL

Equipment and reagents

Both chemicals and instruments have already been described[1]. Salts used in interference studies were of the highest purity available.

Procedure

The effects produced by diverse ions were investigated by maintaining a constant molar ratio of ligand to palladium(II) at 10:1, 11:1 or 11.4:1; these ratios are sufficiently high for the absorbance to be independent of the ligand concentration.

Buffer (3.7 ml of 0.1 *M* potassium hydrogenphthalate–0.1 *M* perchloric acid), and 1.80 ml of an aqueous $0.82 \cdot 10^{-3}$ *M* solution of palladiazo were mixed with the solution containing the diverse ion or ions being studied (anions were used as their sodium or potassium salts and cations as their nitrates, unless otherwise indicated). Then 1.40 ml of palladium(II) solution (10 μg Pd(II) ml^{-1} in 0.05 *M* perchloric acid freshly prepared by dilution of a stock solution[1]) was added. The solution was mixed rapidly (time zero), diluted to volume and thoroughly mixed. The absorbance was measured at 660 nm or 670 nm in matched 10-mm cells, against a blank containing the same concentration of reagent and buffer.

The pH of the test and blank solutions was 2.4±0.1. The absorbance found was compared with the value for an equal amount of palladium(II) measured at an equal time.

INTERFERENCE STUDIES

Effect of chloride

Depending on the medium and the concentration of the cation, chloride forms with palladium(II) one or several of the following complexes in equilibrium$^{2-5}$: $PdCl^+$, $PdCl_2$, $PdCl_3^-$ and $PdCl_4^{2-}$ and relatively strong chloroaquo complexes; accordingly, chloride will probably compete with any other compound reacting with palladium(II). Figure 1 shows that, with 100-fold molar amounts of chloride, there is no interference at any time of measurement. With higher molar ratios of chloride, there is usually interference, except, after 24 h, when the ML_2 complex is measured, when up to 5,000-fold amounts of chloride can be tolerated.

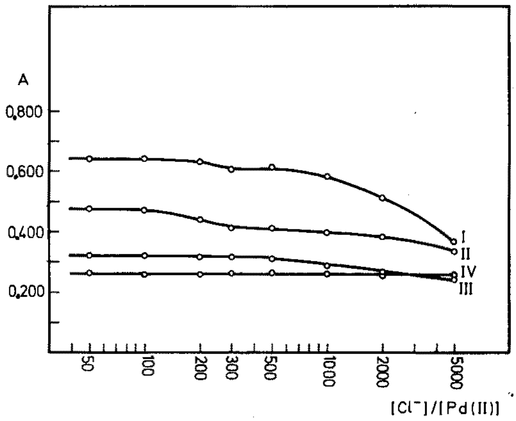

Fig. 1. Influence of chloride concentration on the absorbance of the palladiazo–Pd(II) complexes of analytical interest. $\lambda = 660$ nm; $c_L = 1.5 \cdot 10^{-4}$ *M*; $c_M = 1.5 \cdot 10^{-5}$ *M*. I = 10 min, II = 30 min, III = 90 min, IV = 24 h. pH = 2.4.

Effects produced by other ions

The concentration of an analyte cannot be determined spectrophotometrically with an error less than that of the instrument used at the particular absorbance measured[6]. According to Kirkbright[7], a foreign ion at some particular concentration may usually be considered not to interfere if it consistently produces an error less than twice the standard deviation of the absorbance value obtained in pure solutions. However, attention should be paid to the particular value of the standard deviation of a given measurement which depends on the particular absolute absorbance values measured. Many papers on spectrophotometric determinations only show the difference between the values found in the presence and absence of a foreign ion without any more rigorous criterion.

The concept of interference must be achieved by considering the accuracy required, and by trying to arrive at a general criterion which may be used to compare the system with others. In the present work, the criterion proposed is as follows: any ion or molecule causes interference above a given concentration or molar ratio, when the analytical concentration found differs from the concentration found in the absence of foreign ions by an amount exceeding the relative percentual error in the concentration, corresponding to an absolute photometric error of 1% *T*, calculated as discussed by Ringbom[8] and Ayres[6].

In the present system, this percentual error was found to be 3.1%, 3.5% and 3.6% measuring after 5 min, 3 h and 24 h, respectively[1]. Those ions which interfere at a given concentration, according to the above criterion are asterisked in Table I. It was previously stated[1] that the wavelength and the time of maximal absorbance of the ML_3 complex are 660 nm and 5 min. It was verified that the effects of diverse ions were exactly the same after 5 or 10 min and at 660 nm, or 670 nm, provided that they were compared with the corresponding analytical curve.

THE DISSOLUTION AND SEPARATION OF Pd(II) OF SAMPLES CONTAINING PALLADIUM

Dissolution procedures

The convenience of having palladium(II) in a medium of perchloric acid makes it possible to eliminate many anions and cations from the dissolved sample.

In the Scherrer distillation apparatus[10] with 60% perchloric acid and (1+1) hydrochloric acid in a carbon dioxide stream, the following elements can be collected by volatilization (the numbers in brackets indicate the % of the total content recovered): As(III) (30), As(V) (5), Au (1), B (20), Bi (0.1), Cr(III) (99.7), Ge (50), Hg(I, II) (75), Mn (0.1), Mo (3), Os (100), P (1), Re (100), Ru (99.5), Sb(III, V) (2), Se(IV, VI) (4), Sn(II) (99.8), Sn(IV) (100), Te(IV) (0.5), Te(VI) (0.1), V (0.5). With perchloric acid and 40% hydrobromic acid instead of hydrochloric acid, 100% recovery of the following elements may be obtained[11]: As(III), V, Os, Re, Ru, Sn(III, IV), and Sb(III, V).

Practically all the natural and artificial materials which may contain palladium, may be brought into solution by any of the following procedures.

(a) Fusion at 1,260° with sodium carbonate and graphite, the melt (Iridiosmines) being dissolved in hydrochloric acid[12,13].

(b) Fusion with sodium hydrogen sulphate or peroxide[14].

(c) If the rhodium and iridium content is not too high, the dry method can be avoided, and oxidation with aqua regia, and later 60–70% perchloric acid, can be used. Any risk involved in a direct dissolution of chromium steels[15], bismuth alloys, lead, antimony and hypophosphites[16,17], in perchloric acid can thus be avoided. This procedure can be used to solubilize dental alloys, minerals, calcopyrite, pyrrhotite, pyrite, pentlandite, polyxenes, and lopolites which contain metals of the platinum group[18,19], porpezite[20], sperrylites, copperite, braggite, palladium bismuthides, natural palladium, tellurium bismuthides, etc. If the sample contains silicon or silicates, hydrofluoric acid must be added to the aqua regia, before the perchloric acid; a teflon capsule and evaporation with an infrared lamp are then required. If the sample contains silver in such an amount that silver chloride could be precipitated, palladium would also precipitate; fuming nitric acid should then be used instead of aqua regia[18].

Separation procedures

If palladium is present in amounts above the trace level, it can be separated as its dimethyl-glyoximate by extraction with chloroform in 0.2–0.3 *M* hydrochloric acid[21,22]. Iron(III) prevents quantitative extraction, and must be masked with EDTA. Chloroform is evaporated and the residue treated with nitric and perchloric acid until white fumes are evolved.

Metals of the platinum group, Pt, Rh, Ir and Pd, may be separated together,

TABLE I

INFLUENCE OF DIVERSE IONS ON THE DETERMINATION OF PALLADIUM

(1.40 μg Pd(II) ml^{-1}. Average value of three determinations)

Diverse ion	*Molar ratio (X : Pd)*	*Pd found (μg ml^{-1})*			*Remarks*
		10 min	*2.5 h*	*24 h*	
F^-	10,000	1.37		1.33*	< 2,000-fold does not interfere after 2.5 and 24 h
	5,000	1.48*	1.50*	1.47*	
	3,000	1.48*	1.33	1.40	
	2,000	1.50*	1.35	1.43	
SO_4^{2-}	10,000	1.67*	1.57*	1.57*	< 5,000-fold does not interfere after 24 h
	5,000	1.50*	1.30*	1.40	
	2,000	1.48*	1.30*	1.40	
$H_2PO_4^-$	10,000	1.70*	1.67*	1.60*	< 5,000-fold does not interfere
	5,000	1.47	1.37	1.43	
	2,000	1.47	1.37	1.47	
	1,000	1.43	1.33	1.43	
NO_3^-	20,000	1.43		1.50*	
	1,000	1.40	1.30*	1.43	
Oxalate	4,000	0.10*	0.60*	1.30*	
Citrate	100	1.18*	1.17*	1.20*	
Te(IV)	1.5 mg	0.90*	1.40	1.50*	Te(IV) in $HClO_4$ at pH 2–3; 0.70 μg Pd(II) ml^{-1}, 10 ml
		0.50*	0.77	0.73	
CrO_4^{2-}	500	1.47	2.50*	Precipitate	
	250	1.33	2.27*	Precipitate	
Mg^{2+}	100	0.90*	1.0*	1.17*	
	50	0.90*	1.03*	1.13*	
	100	1.37	1.33	1.37	Measured *vs.* a spectrophotometric blank with the same Mg(II) concentration
Ca^{2+}	100	1.50*	1.57*	1.63*	
	50	1.37	1.37	1.43	
	100	1.37	1.57*	1.50*	Interference eliminated by measuring at 10 min with Ca^{2+} : citrate = 100 : 100
Ba^{2+}	1,000	1.50*	1.56*	1.53*	
	50	1.45	1.53*	1.53*	
Al^{3+}	100	1.57*	1.87*	1.97*	
	50	1.50*	1.63*	1.63*	
	100	1.50*	1.73*	1.90*	Citrate added equimolar with Al^{3+}
	100	1.47	1.97*	2.17*	Citrate added in 2-fold molar amount over Al^{3+}
Ag^+	1,000	1.70*	1.80*	1.73*	
	50	1.57*	1.65*	1.63*	
	20	1.40	1.40	1.40	
Cu^{2+}	1,000	1.80*	2.20*	2.30*	
	100	1.35	1.40	1.40	
Co^{2+}	1,000	1.50*	1.57*	1.63*	
	500	1.50*	1.50*	1.53*	
	250	1.27*	1.30*	1.37	
Ni^{2+}	5,000	2.10*	2.63*	2.73*	
	500	1.50*	1.60*	1.62*	
	250	1.30*	1.37	1.40	

TABLE I (*continued*)

Diverse ion	*Molar ratio (X:Pd)*	*Pd found (µg ml⁻¹)* 10 *min*	2.5 *h*	24 *h*	*Remarks*
Cr^{3+}	500	2.07*	4.7*	Precipitate	Cr(III) ppts. with biphthalate[9]
	25	1.57*	2.73*	Precipitate	
Mn^{2+}	500	1.48*	1.47*	1.40	
	250	1.45	1.43	1.40	
	100	1.38	1.42	1.45	
Fe^{3+}	100	Precipitate			Fe^{3+} ppts. with biphthalate[9].
	50	Precipitate			Citrate or tartrate are ineffective
Ir(IV)	10	2.40*	Precipitate		Ir(IV) in 0.05 *M* $HClO_4$
	5	1.82*	2.28*	2.13*	
	2	1.48*	1.60*	1.73*	
	1	1.42	1.43	1.48*	
Pt(IV)	10	1.45	1.40	1.38	Pt(IV) as $H_2Cl_6Pt \cdot 6H_2O$
	5	1.38	1.40	1.39	
Ru(III)	10	1.47*	2.00*	2.18*	Ru(III) as $RuCl_3$ $1.3 \cdot 10^{-3}$ *M* in 0.1 *M* $HClO_4$
	5	1.40	1.55*	1.58*	
Rh(III)	10	1.62*	1.82*	1.70*	
	5	1.35	1.40	1.38	
Os(VIII)	20	1.52*	1.73*	1.88*	Os(VIII) as OsO_4
	10	1.62*	1.63*	1.72*	
	5	1.62*	1.57*	1.67*	
	2	1.47	1.42	1.42	
Au(III)	20	1.38	1.20*		Must be measured after 5–10 min. Au(III) as $AuCl_3$
	10	1.45	1.23*	0.90*	
	5	1.35	1.68*	1.58*	
Au(III) Pt(II) Rh(III)	2 2 2	1.40	1.48*	1.42	

after distillation of Os and Ru as OsO_4 and RuO_4 with perchloric acid, by means of Dowex 50-X8 resin[13,23]. Pd and Pt may be separated with sodium diethyldithiocarbamate from the rest of the group[24]. Rh and Ir may be separated from palladium by extraction with tributylphosphate, after their conversion to iodides[25].

The extraction of Pd, Pt and Au[26] from minerals by fusion with lead oxide, although quantitative, is more suitable for a subsequent spectrographic analysis. This is also true for the tin button method for the isolation of noble metals[27].

Small amounts (*ca.* 2 µg) of palladium have been separated from 10-fold amounts of platinum by collection with iron(III) hydroxide[28].

Traces of palladium, silver and gold can be coprecipitated with tellurium[29-34]; Pt, Rh and Hg are partially precipitated.

APPLICATIONS OF PALLADIAZO METHOD

Determination of palladium in catalysts and minerals

In order to check the results of the spectrophotometric method, gravimetry with nioxime (1,2-cyclohexanedionedioxime)[35] was used simultaneously. It was found that the lower limit (5 mg Pd)[35] of the latter method could be reduced; on the basis of 10 determinations each, average results of 1.72 ± 0.04 mg of Pd, and 1.00 ± 0.04 mg of

TABLE II

DETERMINATION OF PALLADIUM IN CATALYSTS

(Gravimetric analysis with nioxime and spectrophotometric analysis[1] with palladiazo. $\lambda = 660$ nm; pH $= 2.4 \pm 0.1$; $t = 5$ min)

Sample	*Gravimetry*			*Spectrophotometry*		
	Pd found (mg/10 ml)	*% Pd*	$x-\bar{x}$	*Pd found* ($\mu g\ ml^{-1}$)	*% Pd*	$x-\bar{x}$
Active carbon[a] I	1.51	4.80	+0.18	1.45	4.61	−0.08
				1.47	4.69	0.00
				1.48	4.70	+0.01
	1.45	4.60	−0.02	1.50	4.76	+0.07
	1.40	4.45	+0.17	1.48	4.70	+0.01
II	1.56	4.67	+0.16	1.55	4.65	+0.04
	1.45	4.34	−0.17	1.53	4.58	−0.03
				1.53	4.58	−0.03
				1.54	4.62	+0.01
	1.51	4.52	+0.01	1.54	4.62	+0.01
Silica gel[b]	1.92	0.432	−0.002	1.47	0.441	−0.007
	2.16	0.486	+0.052	1.47	0.441	−0.007
	1.89	0.426	−0.008	1.49	0.451	+0.003
	1.84	0.414	−0.020	1.52	0.456	+0.008
	1.84	0.414	−0.020	1.50	0.450	+0.002
Asbestos[c] I	2.11	4.41	−0.01	1.35	4.71	−0.03
				1.35	4.71	−0.03
	2.09	4.37	−0.05	1.37	4.77	+0.03
				1.35	4.71	−0.03
	2.14	4.48	+0.06	1.38	4.81	+0.07
II	3.37	4.42		1.65	4.41	+0.01
	3.15	4.13		1.66	4.53	+0.03
	3.02	3.96		1.65	4.51	+0.01
	3.24	4.25		1.63	4.45	−0.05
	3.35	4.39		1.65	4.51	+0.01
Kieselguhr[d] I	1.62	5.40	+0.34	1.55	5.17	−0.01
	1.45	4.84	−0.22	1.54	5.14	−0.04
	1.48	4.94	−0.12	1.53	5.10	−0.08
				1.57	5.24	+0.06
				1.57	5.24	+0.06
II	1.67	4.76	−0.13	1.84	5.25	−0.02
	1.78	5.07	+0.18	1.84	5.25	−0.02
	1.70	4.85	−0.04	1.85	5.27	0.00
				1.87	5.33	+0.05

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[a] 5% Pd on active carbon (Fluka A.G.); specific area 1113.2 m^{2}g^{-1}. Dilution for spectrophotometry: 50/10.0, 250/2.50, 10.0. Sample I, 0.1574 g/50 ml; II, 0.1669 g/50 ml.

[b] 0.5% Pd on silica gel (Engelhard Industries, Ltd.); specific area 357.96 m^{2}g^{-1}. In this case only 8 ml of final solution was used for gravimetry. Dilution for spectrophotometry: 50/5.0, 250/3.00, 10.0. Sample, 2.7751 g/50 ml.

[c] 5% Pd on asbestos (Fluka A.G.); specific area 16.99 m^{2}g^{-1}. Dilution for spectrophotometry: I 50/7, 250/1.50, 10.0; II 50/8.0, 100/1.50, 10.0. Sample I, 0.2391 g/50 ml; II, 0.3815 g/50 ml.

[d] 5% Pd on Kieselguhr (Fluka A.G.); specific area 32.17 m^{2}g^{-1}. Dilution for spectrophotometry: 50/10.0, 250/2.50, 10.0. Sample I, 0.1499 g/50 ml; II, 0.1754 g/50 ml.

Pd were achieved with relative errors of ±2.1% and ±4.4% respectively[36].

As a rule, two parallel analyses of each catalyst were carried out, the palladium contents being determined both gravimetrically and spectrophotometrically with palladiazo[1].

Procedure for palladium on active carbon. Place the sample (*ca.* 0.15 g) in a 50-ml round-bottom flask, and add 15 ml of 70% perchloric acid and 5 ml of 65% nitric acid. Fix a reflux condenser in position (ground-glass joints) and heat gently at the start. Then boil for 3 h. This treatment completely oxidizes carbon and a clear liquid is obtained. Fit a Claisen head with a closed side tube, and boil almost to dryness. Allow to cool and add 4 ml of 70% perchloric acid. Reduce the volume by one half, and then dilute with water to 50 ml. If, during the final evaporation, dark deposits form on the walls, stop heating and add a few ml of aqua regia; then proceed as previously indicated. A red precipitate may appear (a palladium perchlorate which is soluble on cooling and diluting).

The weight of the sample may be reduced to 70–80 mg, if only the spectrophotometric analysis is used; the solution is then diluted to 500 ml, 4 ml of 70% perchloric acid being added previously to the flask. Use 2.0–3.0 ml for the spectrophotometric analysis in 10-ml volumetric flasks. Table II shows the results obtained.

Procedure for palladium on silica gel catalyst. Place the sample (*ca.* 2.8 g) in a

TABLE III

DETERMINATION OF PALLADIUM IN CALCIUM CARBONATE CATALYSTS

Sample	*Gravimetry*			*Spectrophotometry*		
	Pd found (mg/5 ml)	*% Pd*	$x-\bar{x}$	*Pd found (μg/ml)*	*% Pd*	$x-\bar{x}$
5% Pd[a,b]	2.55	5.09	+0.19	1.50	5.00	−0.03
	2.47	4.94	+0.04	1.50	5.00	−0.03
	2.37	4.74	−0.16	1.50	5.00	−0.03
	2.63	5.25	+0.35	1.55	5.16	+0.13
	2.30	4.60	−0.30	1.50	5.00	−0.03
	2.36	4.72	−0.18			
10% Pd[c] I[d]	1.62	9.91	+0.11	1.63	10.39	+0.20
	1.65	10.10	+0.30	1.55	9.88	−0.31
	1.59	9.73	−0.07	1.58	10.07	−0.12
	1.59	9.73	−0.07	1.60	10.20	+0.01
	1.56	9.55	−0.25	1.63	10.39	+0.20
II[d,e]	2.99	10.02	+0.26	1.45	10.12	−0.14
	2.83	9.48	−0.28	1.47	10.26	0.00
	2.91	9.75	−0.01	1.45	10.12	−0.14
	2.96	9.92	+0.16	1.50	10.47	+0.21
	2.88	9.65	−0.11	1.48	10.33	+0.07

[a] Nominal 5% Pd (Fluka A.G.); specific area 7.92 m^2g^{-1}. Sample of 1.001 g/100 ml taken.

[b] For spectrophotometry, the dilutions were: 100/5.00, 500/3.00, 10.0. When the dilutions were 100/1.00, 500/3.00, 10, an average result of 4.82%±0.06% Pd was obtained.

[c] Nominal 10% Pd (Fluka A.G.); specific area 10.63 m^2g^{-1}. Sample of 0.3268 g/100 ml taken.

[d] Dilutions for spectrophotometry were: 100/8.00, 500/3.00, 10.0. Sample 0.2985 g/100 ml.

[e] 10-ml aliquots taken for gravimetry instead of 5 ml.

TABLE IV

STATISTICAL SURVEY OF THE RESULTS FOR PALLADIUM IN CATALYSTS

Support	*Nominal content in Pd(%)*	*Gravimetry*			*Spectrophotometry with palladiazo*		
		S^a	$S_R{}^b$ (%)	$\Sigma/n \pm 2S/N^{\frac{1}{2}}$	S	S_R (%)	$\Sigma/n \pm 2S/N^{\frac{1}{2}}$
Active carbon	5	0.13	±2	4.6±0.2	0.06	±0.5	4.65±0.05
Silica gel	0.5	0.03	±5	0.43±0.04	0.006	±2	0.448±0.008
Asbestos	5	0.18	±3	4.3±0.2	0.04	±0.5	4.62±0.03
Kieselguhr	5	0.27	±4	5.0±0.3	0.07	±0.5	5.23±0.05
Calcium carbonate	5	0.26	±3	4.9±0.2	0.13	±1	4.93±0.09
	10	0.22	±1	9.8±0.3	0.18	±1	10.2±0.1

[a] Standard deviation.
[b] Relative standard deviation.

100-ml Teflon capsule, and add 5 ml of 65% nitric acid, 10 ml of 50% hydrofluoric acid ($d = 1.15$) and 10 ml of 70% perchloric acid. When the initial reaction ceases, heat the mixture under an infrared lamp with slow stirring until the volume is reduced to 8–10 ml. Transfer the contents to a 100-ml beaker with aqua regia, and continue heating on a hot plate until the mixture is almost dry. Allow to cool and add 10 ml of 70% perchloric acid. Reduce the volume to 4–5 ml, cool and dilute to 50 ml.

If only the spectrophotometric analysis is needed, take a 350-mg sample, and dilute the final solution to 250 ml.

Table II shows the results obtained.

Procedure for palladium on asbestos. Use a sample of 0.24–0.32 g and treat in the same way as the silica gel catalyst. When the volume is reduced to 4–5 ml, prisms of sodium and magnesium perchlorates form, but these readily dissolve on dilution of the cold mixture.

The sample was very heterogeneous and difficult to homogenize, owing to the nature of the support; the deposit of palladium proved to be very easily detached from the support. The results obtained are included in Table II.

Procedure for palladium on Kieselguhr. Use samples of *ca.* 0.15 g and treat in the same way as the silica gel catalyst.

A typical Kieselguhr or siliceous earth analysis shows the following composition[37]: 82.54% SiO_2, 6.58% Al_2O_3, 1.93% Fe_2O_3, 2.66% CaO, loss on ignition 5.37%. The results obtained for palladium are included in Table II.

Procedure for palladium on calcium carbonate. Weigh the sample (0.3–1 g) into a 100-ml beaker, and add 10 ml of water and 10 ml of aqua regia, avoiding spurting. When evolution of carbon dioxide ceases, heat the mixture (very gently initially), and evaporate almost to dryness. Cool, add 20 ml of 70% perchloric acid, again evaporate almost to dryness, cool and dilute to 100 ml.

In all cases, during dilution of freshly prepared solutions, the perchloric acid concentration was maintained above 0.05 *M*. In order to determine palladium by spectrophotometry only, amounts of sample of 70–80 mg can be weighed. Table III shows results obtained with 5% and 10% palladium catalysts.

Table IV shows a statistical survey of the results obtained for different catalysts.

The confidence interval and the relative error were calculated for a 95% probability level[38]. The gravimetric and spectrophotometric results show excellent agreement. The small difference observed for asbestos and Kieselguhr supports probably derives from the presence of large amounts of magnesium. This difference in the spectrophotometric determination can be overcome by adding the same amount of magnesium to the spectrophotometric blank (see Table I).

Determination of palladium in minerals

Three samples originating from Sudbury (Canada) were analysed: pyrrhotite, pentlandite and calcopyrite.

Pyrrhotite contains 0.99–1.76 p.p.m. of metals belonging to the platinum group, pentlandite contains an average 5.4 p.p.m. and calcopyrite contains an average 7.7 p.p.m.[39]. The contents of palladium are 48.7%, 64.6% and 71.5%, respectively, on the basis of the total contents of platinum group metals[39]. A discussion on the non-interference of other minor metals of this group, and silver, in the spectrophotometric determination of palladium with palladiazo has been given elsewhere[36]. The investigated minerals were available as three compact solid pieces (*ca.* 100 g each), macroscopically almost homogeneous. These pieces were broken into small portions, and then powdered first in a ball grinder, and then in an agate mortar, to a particle size of 125 μm.

Procedure. Weigh the sample (22.562 g of pentlandite, 30.114 g of pyrrhotite and 41.347 g of calcopyrite were taken) into a 1-l Erlenmeyer flask, and add 50 ml of water and 200 ml of concentrated hydrochloric acid (37%; $d = 1.19$), stirring manually until the hydrogen sulphide evolution ceases. Place a funnel in the neck of the flask to avoid spurting, and boil for 3 h. Add hydrochloric acid occasionally to replace the evaporated acid. Allow to cool and slowly add 250 ml of freshly prepared aqua regia. Add some anti-bumping granules and boil until the volume is reduced to 80–100 ml. If it is necessary to oxidize a small residual amount of sulphur, add another 250-ml amount of aqua regia. Finally add 250 ml of concentrated hydrochloric acid and boil the mixture until the volume has been reduced to *ca.* 100 ml.

Allow the mixture to cool, and filter the residue using glass sintered or porcelain filter-plate funnels (porosity 3) under vacuum. Transfer the contents of the filter flask to a 1-l volumetric flask, washing the funnel, the flask and filter flask with 210 ml of 6 *M* hydrochloric acid and diluting to the mark with water.

[The following points should be noted. The sample attack must be made in a well ventilated hood. The preliminary hydrochloric acid treatment helps to avoid massive formation of sulphur, which would occur if the attack were made directly with aqua regia. Sulphur, which is formed in small amounts, is totally oxidized with boiling aqua regia, which also completes the dissolution of the residual mineral. Heating must be carried out uniformly.

A constant-boiling mixture of hydrochloric acid and water (20.24% (w/w) HCl, $d = 1.09$) is obtained when the volume of the solution is reduced by evaporation; this evaporation also eliminates nitric acid. The final addition of hydrochloric acid gives a convenient acidity (2–3 *M*) for the separation of palladium.

Filtration yields a small gray residue, which is insoluble in boiling aqua regia, but is slightly cleared in colour by calcination. This residue apparently consists of silicates and silica; the absence of palladium was verified. It may contain rhodium and iridium, since they are insoluble in aqua regia; the residue can be solubilized by fusion with a potassium hydrogensulphate–carbonate flux in order to check for these metals.]

After dilution of the filtrate to 1 l, divide the solution into two 500-ml portions accurately and quantitatively transfer each portion to 1-l glass beakers with water. Treat each solution as follows.

Add 20 ml of tellurium(IV) solution (1 mg/ml) in 2 *M* hydrochloric acid with constant stirring. (To prepare the solution, treat 250 mg of tellurium with 4 ml of concentrated nitric acid, evaporate to dryness, dissolve the residue in 40 ml of concentrated nitric acid and dilute with water to 250 ml.) Then add 100 ml of 20% tin(II) chloride dihydrate solution with constant stirring. Boil until precipitate coagulates, checking for complete precipitation in a portion of the supernate. Filter the precipitate under suction on a porosity 3 filter funnel, washing with cold 1 *M* hydrochloric acid until a drop of the filtrate shows a negative test for iron(III) or copper(II). Slowly add 20–30 ml of concentrated nitric acid over the precipitate without suction. When the precipitate has dissolved, add 10–15 ml of concentrated hydrochloric acid and allow the mixture to stand for a few minutes. Apply suction and wash the plate with small portions of aqua regia. Quantitatively transfer the solution (50–60 ml) to a 250-ml beaker, and carefully evaporate to 5–10 ml. Transfer this solution quantitatively to a crucible with small portions of hot concentrated nitric acid. Evaporate to dryness, cool and add 2–3 g of ammonium iodide. Heat the mixture over a Meker burner until TeO_2 is completely volatilized. Repeat the treatment with ammonium iodide 2–3 times. Allow the crucible to cool and add 5 ml of aqua regia and 5 ml of 60% perchloric acid. Evaporate to a final volume of *ca.* 0.5 ml by boiling, allow to cool and dilute with 2–3 ml of water. Adjust the pH to 1–1.5 by dropwise addition of sodium hydroxide solution, using small electrodes. Transfer the contents of the crucible to a 25-ml volumetric flask using water to rinse. Finally, dilute the solution to the mark and check for the absence of iron(III) with hexacyanoferrate(II).

Transfer a 4- or 5-ml aliquot portion to a 10-ml volumetric flask, add 3 ml of potassium hydrogenphthalate–perchloric acid buffer and 1.40 ml of palladiazo reagent ($1.09 \cdot 10^{-3}$ *M*), and measure the absorbance after 5 min at 660 nm against a reagent blank.

Results. It was verified that the pH ranged between 2.4 and 3 in all cases. Triplicate spectrophotometric determinations were carried out, the collection with tellurium being repeated twice, as indicated, for each mineral. The average values for palladium were shown to be 3.8 p.p.m. (calcopyrite), 2.0 (pentlandite) and 0.28 (pyrrhotite).

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SUMMARY

The interference characteristics derived from the presence of 30 cations and 8 anions in the 1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis[(azophenylene-*p*-arsonic)]–Pd$(H_2O)_4^{2+}$ spectrophotometric system have been investigated; the system is practically free of interferences. The method is applied to the determination of palladium in several catalysts and minerals; gravimetric determinations with nioxime were used as parallel checks. The reproducibility and agreement of the results obtained by the two methods are excellent.

RÉSUMÉ

On examine l'influence de 30 cations et 8 anions dans le système spectrophotométrique dihydroxy-1,8-naphtalène disulfo-3,6-bis[(azophénylène-*p*-arsonique)] 2,7–Pd$(H_2O)_4^{2+}$. On n'observe pratiquement aucune interférence. Cette méthode peut être appliquée au dosage du palladium dans divers catalyseurs et minéraux. Des essais parallèles sont effectués avec la nioxime. Les résultats obtenus par ces 2 méthodes sont excellents et concordent parfaitement bien.

ZUSAMMENFASSUNG

Das spektrophotometrische System Palladiazo–Pd$(H_2O)_4^{2+}$ wurde im Hinblick auf Störungen durch die Gegenwart von 30 Kationen und 8 Anionen untersucht. Es zeigte sich, dass das System praktisch störungsfrei ist. Die Methode wird auf die Bestimmung von Palladium in verschiedenen Katalysatoren und Mineralen angewendet; zur Kontrolle wurden gravimetrische Parallelbestimmungen mit Nioxim ausgeführt. Die Reproduzierbarkeit und die Übereinstimmung der nach den beiden Methoden erhaltenen Ergebnisse sind ausgezeichnet.

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DISMUTATION REVERSIBLE DE UO_2(V) DANS LES CHLORURES FONDUS

INFLUENCE DE LA TEMPÉRATURE ET DE LA COMPOSITION DU SOLVANT

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Dans deux articles précédents[1,2], nous avons examiné la dismutation réversible de UO_2(V) dans l'eutectique LiCl–KCl à 450° et nous sommes arrivés à la conclusion que les résultats se laissent interpréter de la façon la plus satisfaisante en admettant essentiellement l'intervention des deux équilibres suivants:

$$2\,UO_2^+ + 2\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,OH^- + 2\,Cl^- \quad (1)$$

$$2\,UO_2^+ + 6\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_3O^+ + 6\,Cl^- \quad (2)$$

le premier équilibre étant prépondérant aux basses pressions en HCl, le second aux hautes pressions; la dissociation de H_2O en H_3O^+ et OH^- semble importante.

Dans cette partie, nous étudions l'influence de la température et de la composition du solvant sur la dismutation réversible de UO_2(V). Nous nous bornerons à faire des mesures dans le domaine où la précision est bonne, notre but étant de cerner uniquement les phénomènes au niveau de la dismutation de l'uranium et non plus de déterminer la répartition des différentes formes de l'eau.

PARTIE EXPÉRIMENTALE

Le dispositif expérimental, les réactifs ainsi que les différentes manipulations ont été décrits précédemment[1-4].

Les mesures ont été effectuées au moyen d'un spectrophotomètre Cary 14 H sur les quatre bains suivants, aux températures indiquées:

1. Eutectique LiCl–KCl: 400, 450, 500°
2. LiCl–KCl (70–30 % mol.): 455, 500°
3. LiCl–CsCl (55–45 % mol.): 400, 450, 500°
4. Eutectique NaCl–KCl–$MgCl_2$: 450, 500°

Détermination des concentrations en U(IV), UO_2(V) et UO_2(VI)

La méthode, basée sur la spectrophotométrie d'absorption du bain fondu, a été exposée antérieurement[1]; comme nous l'avons vu, il s'agit d'abord de déterminer les coefficients d'extinction molaire ε_4 de U(IV) au maximum de la bande situé vers 1105–1160 nm et ε_5 de UO_2(V) au maximum de la bande situé vers 1517–1535 nm. Nous avons montré précédemment[3] que la loi de Beer est vérifiée pour U(IV) à 450° au maximum de la bande à 1160 nm dans l'eutectique LiCl–KCl et à 1105 nm dans le

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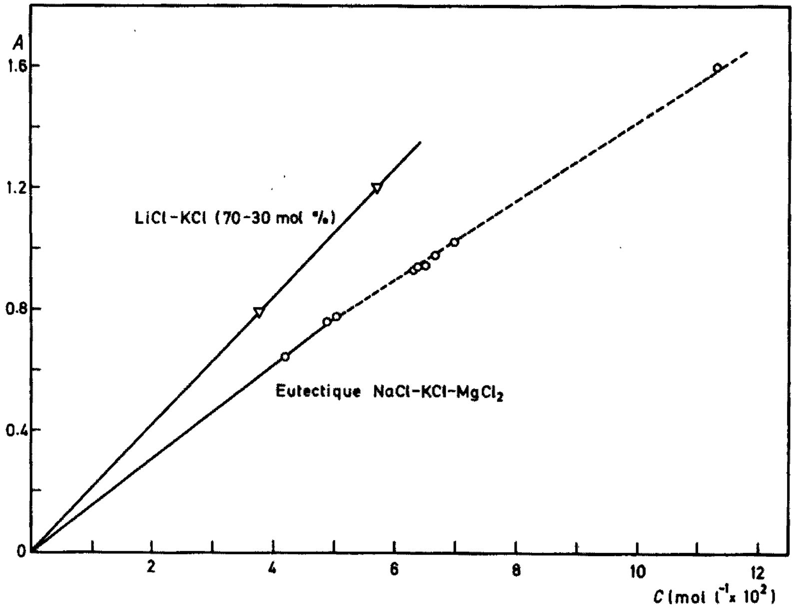

Fig. 1. Vérification de la loi de Beer–Lambert pour les bandes de U(IV) à 1160 nm dans LiCl–KCl (70–30 % mol.) à 455° et à 1106 nm dans l'eutectique NaCl–KCl–$MgCl_2$ à 450°.

bain LiCl–CsCl; la Fig. 1 montre qu'il en est de même pour le bain LiCl–KCl (70–30) alors que dans l'eutectique ternaire, il y a des écarts lorsque la concentration en U(IV) dépasse $5 \cdot 10^{-2}$ mole l^{-1}; nous nous sommes efforcés de travailler dans le domaine de la linéarité. Ces courbes d'étalonnage ont permis de calculer ε_4 pour les quatre bains considérés à 450° ; les valeurs aux autres températures sont calculées sur la base de la dilatation thermique du solvant:

$$\varepsilon_t = \varepsilon_{450} \frac{A_t}{A_{450}} \frac{C_{450}}{C_t} \tag{3}$$

ε_t, ε_{450} = coefficients d'extinction molaires aux températures t et 450°.
A_t,A_{450} = absorbances au maximum à t° ou 450° pour des solutions de concentrations C_t et C_{450}.

Si les deux mesures d'absorbance se font sur la même solution, C_{450}/C_t est égal au rapport des poids spécifiques.

Comme précédemment[1], les valeurs de ε_5 de UO_2(V) au maximum de la bande vers 1517–1535 nm ont été obtenues à partir de la relation

$$\varepsilon_5 = -\frac{\varepsilon_4}{2} \frac{\Delta A_5^{1535}}{\Delta A_4^{1160}} \tag{4}$$

Le Tableau I contient les valeurs obtenues pour ε_4 et ε_5 dans ces différents bains, aux différentes températures.

Les valeurs de y et z nécessaires pour le calcul des concentrations des différentes espèces d'uranium, suivant la méthode antérieurement exposée[1] et représentant respectivement les absorbances de U(IV) à 1310 nm et au maximum de la bande de UO_2(V) vers 1517–1535 nm, se trouvent également dans le Tableau I sous forme de

TABLEAU I

VALEURS DE ε_4 ET ε_5 DANS LES DIFFÉRENTS BAINS

Solvant	$t(°)$	λ_{max} (*nm*)	ε_4 ($l\ mol^{-1}\ cm^{-1}$)	ε_{max} (*nm*)	ε_5 ($l\ mol^{-1}\ cm^{-1}$)	$\frac{y}{A_4}$	$\frac{x}{A_4}$	$-\frac{\Delta A_5}{\Delta A_4}$	$\frac{A_t}{A_{450}}$	$\frac{C_{450}}{C_t}$
Eutectique	400		20.4		20.8	0.129	0.222	2.04	1.107	0.984
LiCl–KCl	450	1160	18.75	1535	19.1	0.126	0.200	2.04	1	1
	500		17.1		17.8	0.139	0.223	2.10	0.897	1.016
LiCl–KCl	455	1160	21.2	1535	22.1	0.140	0.206	2.08	1	1
(70–30 % mol.)	500		19.8		20.6	0.153	0.204	2.08	0.921	1.014
LiCl–CsCl	400		10.5		8.5	0.115	0.200	1.62	1.026	0.983
(55–45 % mol.)	450	1105	10.4	1535	8.4	0.130	0.193	1.62	1	1
	500		10.3		8.3	0.148	0.200	1.62	0.976	1.018
Eutectique	450	1106	15.5	1517	26.7	0.208	0.193	3.45	1	1
NaCl–KCl–$MgCl_2$	500		14.8		22.2	0.231	0.196	2.95	0.934	1.021

y/A_4 et z/A_4 (A_4 représentant l'absorbance de la même solution au maximum situé vers 1105–1160 nm).

Il y a lieu cependant de faire deux remarques: la première concerne la détermination des valeurs de ε_5 à partir de la formule (4): pour les deux bains LiCl–KCl (70–30) et LiCl–CsCl (55–45), on a préféré conserver aux autres températures, la valeur déterminée à 455 et 450° ; la dispersion des points expérimentaux à ces températures était en effet telle que les valeurs obtenues paraissaient douteuses. La deuxième remarque concerne l'eutectique ternaire ; à l'encontre de ce qui se passe dans les autres solvants étudiés, on ne peut plus admettre que le coefficient d'extinction de $UO_2(V)$ au maximum de la bande de U(IV) vers 1106 nm où l'on mesure A_4 soit négligeable. Dans ce cas, la méthode utilisée pour arriver à déterminer les concentrations des différentes espèces d'uranium est la suivante: on peut, sur un spectre de $UO_2(V)$, mesurer le rapport des absorbances de $UO_2(V)$ aux deux longueurs d'onde 1106 et 1517 nm, soit

$$\frac{\varepsilon_5^{1106}}{\varepsilon_5^{1517}} = 0.015 \text{ à } 450°$$

Dans ces conditions, on peut écrire, sans trop d'erreur, que

$$A_5^{1106} = 0.015\ y' \tag{5}$$

Or, comme il est indiqué sur la Fig. 2,

$$A_4 = x + y - A_5^{1106} = x + y - 0.015\ y' \tag{6}$$

D'autre part,

$$y = 0.208\ A_4 \tag{7}$$

D'où

$$A_4 = 1.263(x - 0.015\ y') \tag{8}$$

On peut donc, en mesurant x et y', calculer A_4^{1106}, c'est-à-dire la concentration en U(IV) et en même temps tracer la ligne de base, puisque la relation (7) permet de calculer y. La détermination de A_5 et de $[UO_2(V)]$ qui en résulte se fait comme précédemment[1]. Notons qu'à 500°, la valeur de $\varepsilon_5^{1106}/\varepsilon_5^{1517} = 0.031$.

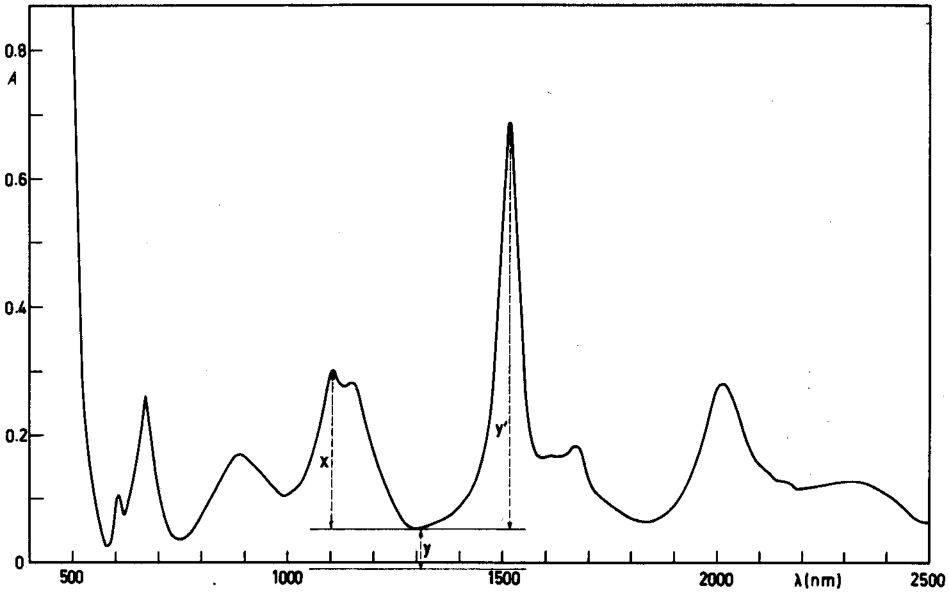

Fig. 2. Mode de dépouillement des spectres de solutions contenant U(IV), UO_2(V) et UO_2(VI) en équilibre de dismutation dans l'eutectique NaCl–KCl–$MgCl_2$.

RÉSULTATS EXPÉRIMENTAUX

Les résultats expérimentaux sont classés par ordre de solvant et de température dans les Tableaux II à V. A partir de ces données, on dresse les diagrammes des Fig. 3 à 6 qui représentent le degré d'avancement de la réaction de dismutation (log $L = [UO_2^{2+}][U^{4+}]^3/[UO_2^{+}]^2$) en fonction du logarithme de la pression en HCl.

Dans le cas de l'eutectique LiCl–KCl à 500°, une seule série de mesures (désignée par des carrés pleins sur la Fig. 3) a été réalisée sans avoir de dégagement de vapeur d'eau. Les autres points doivent être situés trop à droite à cause d'une perte d'eau du bain qui n'a pas été évaluée (L calculé trop élevé).

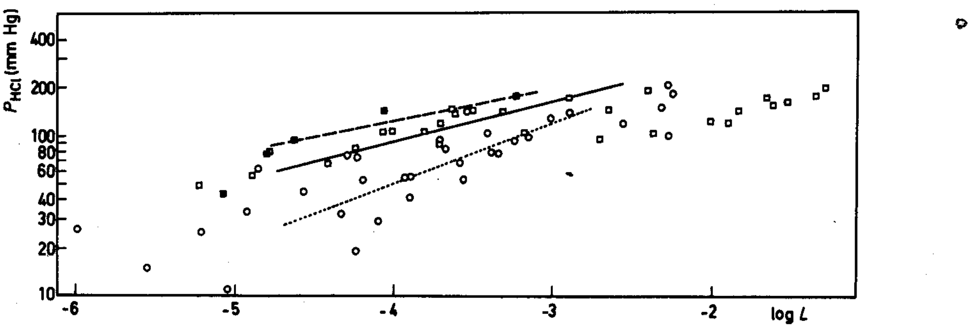

Fig. 3. Détermination du degré d'avancement (log L=log $[UO_2^{2+}][U^{4+}]^3/[UO_2^{+}]^2$) de la réaction de dismutation en fonction de la pression en HCl dans l'eutectique LiCl–KCl à (○---○) 400 et (□ ■---) 500°. Les points expérimentaux à 450° (———) ont déjà été publiés[1].

TABLEAU II

EUTECTIQUE LiCl–KCl

Exp. + t°	$C_{Tot.}$ (*mole* l^{-1})	P_{HCl} (*mm Hg*)	*U(IV)* (*mole* $l^{-1} \cdot 100$)	$UO_2(V)$ (*mole* $l^{-1} \cdot 100$)	$-\log L$
No. 23	0.1102	200	1.62	0.80	2.24
400°		177	1.66	0.80	2.21
		147	1.64	0.85	2.28
		114	1.52	0.99	2.52
		91.5	0.92	1.08	3.22
		79	0.85	1.13	3.37
		67	0.76	1.22	3.57
		55	0.62	1.36	3.92
		44.5	0.39	1.42	4.57
		34	0.29	1.36	4.92
		25	0.23	1.37	5.21
		15	0.18	1.4	5.55
No. 28	0.1621	128	1	1.17	2.99
400°		97	0.96	1.29	3.13
		77.5	0.91	1.49	3.33
		53.5	0.85	1.72	3.55
		55.5	0.56	1.37	3.89
		41	0.55	1.37	3.89
		29.5	0.49	1.44	4.09
		19	0.45	1.50	4.24
No. 41	0.0847	102	0.46	0.87	4.04
400°		64	0.31	1.22	4.85
		27	0.16	1.64	6.00
		140	0.45	0.48	3.52
		75	0.34	0.75	4.28
		137	1.63	1.33	2.87
		91.5	1.25	2.22	3.7
		73	0.54	1.33	4.23
		104	1.29	1.69	3.39
		81	1.17	1.97	3.66
		52	0.71	1.82	4.19
		32	0.63	1.79	4.33
No. 26	0.1331	171	3.89	0.99	1.30
500°		175	2.77	0.93	1.62
		148	2.56	1.02	1.80
		128	2.44	1.15	1.97
		106	1.94	1.27	2.34
		99	1.43	1.21	2.68
		204	4.31	1.04	1.23
		161	3.80	1.30	1.57
		126.5	3.35	1.51	1.85
		172	4.23	1.33	1.48
No. 27	0.0984	190	1.11	1.28	3.21
500°		147.5	0.82	2.06	4.05
		99	0.46	1.76	4.62
		79.5	0.41	1.83	4.80
		58.5	0.39	1.87	4.89
		46.5	0.34	1.87	5.06
		194	2.04	1.14	2.36
		146	1.82	1.29	2.62

(*Continué sur la page* 266)

TABLEAU II (*continué*)

Exp. + t°	$C_{\text{Tot.}}$ (*mole* l^{-1})	P_{HCl} (*mm Hg*)	*U(IV)* (*mole* $l^{-1}\cdot 100$)	$UO_2(V)$ (*mole* $l^{-1}\cdot 100$)	*−log L*
		104.5	1.32	1.53	3.16
		92	0.75	1.29	3.70
No. 28	0.1570	150.5	1.12	2.29	3.48
500°		127.5	0.96	2.35	3.70
		142	1.13	2.62	3.60
		110.5	0.92	3.01	3.99
		86.5	0.78	3.10	4.24
		68	0.68	3.11	4.41
		177	1.77	2.19	2.87
		146	1.30	2.28	3.29
		109	0.91	2.40	3.8
		150.5	0.88	1.93	3.62
		108	0.67	2.10	4.05
		80.5	0.37	2.07	4.80
		50.5	0.27	2.09	5.22

TABLEAU III

LiCl–KCl (70–30% mol.)

Exp. + t°	$C_{\text{Tot.}}$ (*mole* l^{-1})	P_{HCl} (*mm Hg*)	*U(IV)* (*mole* $l^{-1}\cdot 100$)	$UO_2(V)$ (*mole* $l^{-1}\cdot 100$)	*−log L*
No. 30	0.0970	167	0.56	1.98	4.49
455°		119	0.38	2.17	5.08
		93	0.26	2.22	5.58
		62.5	0.23	2.21	5.74
		110	0.22	2.04	5.72
		53.5	0.06	2.15	7.45
		128	0.20	1.81	5.72
		238	0.47	1.56	4.48
		193	0.39	1.72	4.82
		134	0.27	1.86	5.37
		99.5	0.22	1.91	5.66
		51	0.11	1.97	6.58
		210	0.42	1.70	4.71
		132.5	0.27	1.92	5.4
		70	0.17	2.10	6.08
No. 30	0.0956	216	1.03	2.51	3.98
500°		176	0.78	3.00	4.51
		127.5	0.53	3.08	5.03
		127.5	0.12	1.99	6.48
		125	0.07	2.08	7.22
		309	0.36	1.19	4.58
		252	0.17	1.05	5.43
		760	1.16	1.67	3.42
		160	0.45	2.87	5.16
		160	0.31	2.26	5.39

TABLEAU IV

LiCl–CsCl (55–45% mol.)

Exp. + t°	$C_{Tot.}$ (*mole* l^{-1})	P_{HCl} (*mm Hg*)	$U(IV)$ (*mole* $l^{-1}\cdot 100$)	$UO_2(V)$ (*mole* $l^{-1}\cdot 100$)	$-\log L$
No. 50	0.0707	17	1.63	1.06	2.77
450°		17	1.62	1.08	2.80
No. 51	0.2028	83	1.92	1.26	2.12
450°		21	1.28	1.58	2.82
No. 52	0.2186	76	2.77	1.95	2.02
450°		28	2.45	2.89	2.54
		32	2.46	2.81	2.51
		21	2.00	3.10	2.85
No. 53	0.2005	164	2.24	0.44	0.995
450°		106	2.15	0.67	1.42
		42	1.83	1.62	2.41
		19	1.55	2.48	3.01
No. 53	0.2041	184.5	2.26	0.27	0.55
400°		101	2.22	0.33	0.74
		60.5	2.15	0.69	1.43
		40	1.93	1.08	1.97
		26	1.84	1.52	2.34
		20	1.72	1.92	2.64
No. 53	0.1970	109	1.96	1.00	1.90
500°		77	1.86	1.39	2.26
		58	1.77	1.73	2.52
		36	1.60	2.10	2.82
		21	1.54	2.37	2.99

Les valeurs de n (coefficient stoechiométrique de HCl dans l'expression générale $2\ UO_2^+ + n\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\ W + n\,Cl^-$) obtenues à partir des pentes des droites calculées par la méthode des moindres carrés, sont reproduites dans le Tableau VI. Etant donné la valeur de ces pentes, on peut conclure que, dans le domaine de reproductibilité tout au moins, les phénomènes observés obéissent en ordre principal à l'équilibre

$$2\ UO_2^+ + 6\ HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\ H_3O^+ + 6\ Cl^-$$

dans l'eutectique ternaire NaCl–KCl–MgCl$_2$, à l'équilibre

$$2\ UO_2^+ + 4\ HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\ H_2O + 4\ Cl^-$$

dans LiCl–KCl (eutectique et mélange 70–30 % mol.) et à l'équilibre

$$2\ UO_2^+ + 2\ HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\ OH^- + 2\ Cl^-$$

dans LiCl–CsCl (55–45).

Cette dernière conclusion trouve une confirmation supplémentaire dans le fait que lors du traitement de $UO_2(VI)$ par l'hydrogène dans LiCl–CsCl (55–45), il se forme, à côté de $UO_2(V)$, des quantités appréciables de U(IV) qui proviennent des réactions successives:

$$2\ UO_2^{2+} + H_2 + 2\ Cl^- \rightarrow 2\ UO_2^+ + 2\ HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\ OH^- + 2\ Cl^-$$

La concentration en HCl formé, combinée à l'effet de la remarquable stabilité

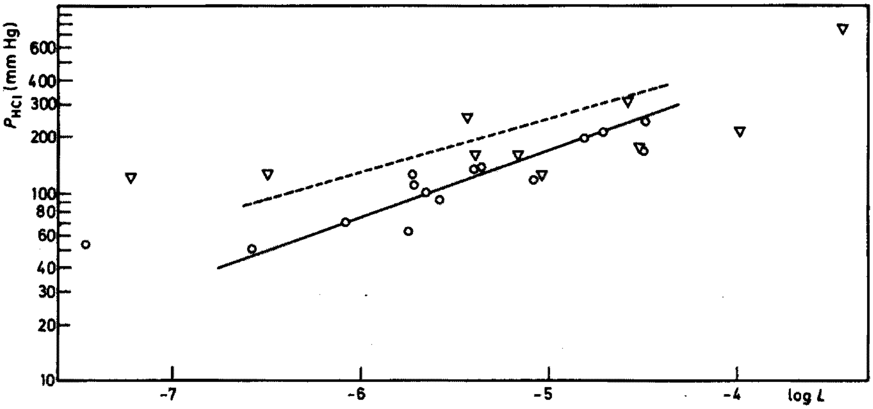

Fig. 4. Détermination du degré d'avancement de la réaction de dismutation en fonction de la pression en HCl dans LiCl–KCl (70–30 % mol.) à (○—○) 455 et (▽---▽) 500°.

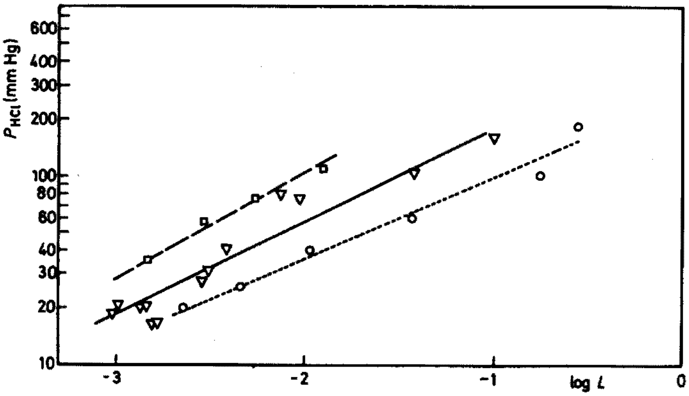

Fig. 5. Détermination du degré d'avancement de la réaction de dismutation en fonction de la pression en HCl dans LiCl–CsCl (55–45 % mol.) à (○---○) 400, (▽—▽) 450 et (□--□) 500°.

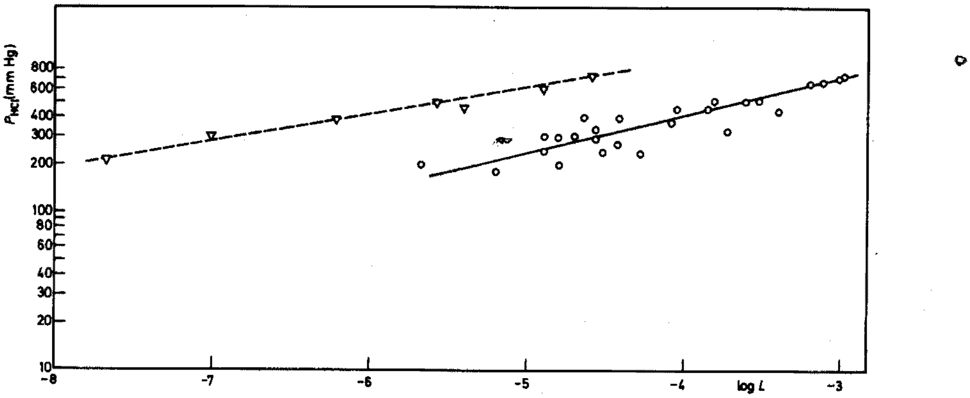

Fig. 6. Détermination du degré d'avancement de la réaction de dismutation en fonction de la pression en HCl dans l'eutectique NaCl–KCl–$MgCl_2$ à (○—○) 450 et (▽--▽) 500°.

TABLEAU V

EUTECTIQUE NaCl–KCl–MgCl$_2$

Exp. + t°	$C_{\mathrm{Tot.}}$ (*mole* l^{-1})	P_{HCl} (*mm Hg*)	$U(IV)$ (*mole* $l^{-1} \cdot 100$)	$UO_2(V)$ (*mole* $l^{-1} \cdot 100$)	$-\log L$
No. 64 450°	0.2178	685	1.99	4.05	3.12
		298	0.61	4.84	4.80
		342	0.67	4.33	4.57
		243	0.53	4.46	4.89
		441	1.80	4.73	3.40
		332	1.51	5.26	3.72
		239	1.09	6.04	4.28
		244	0.77	4.93	4.52
No. 65 450°	0.1516	658	1.86	3.18	3.19
		455	1.37	4.21	3.85
		455	1.15	4.13	4.05
		303	0.68	4.06	4.7
		180	0.43	3.74	5.2
		510.5	1.68	3.92	3.53
		373	1.26	4.73	4.09
		272	0.85	4.09	4.43
No. 66 450°	0.1188	711	1.95	2.41	3.02
		517	1.57	3.32	3.61
		404	0.89	4.46	4.64
		305	0.79	4.91	4.89
		199	0.38	4.34	5.68
		760	2.04	2.46	2.98
		510	1.49	3.79	3.82
		402	1.02	4.28	4.42
		291	0.74	3.42	4.57
		200	0.65	3.63	4.80
No. 67 500°	0.0637	745	0.67	2.06	4.58
		498	0.39	2.68	5.57
		390	0.26	3.00	6.21
		306	0.15	3.22	7.01
		214	0.09	3.24	7.68
		615	0.57	2.27	4.90
		464	0.43	2.59	5.40

TABLEAU VI

COEFFICIENTS STOECHIOMÉTRIQUES DE HCl

Solvant	*Température*	*n*	*Ecart type*
Eutectique LiCl–KCl	400	2.72	0.32
	450	3.70	0.19
	500	5.5	0.8
LiCl–KCl (70–30 % mol.)	455	2.6	0.6
	500	3.3	1.2
LiCl–CsCl (55–45 % mol.)	400	2.31	0.19
	450	1.72	0.17
	500	1.51	0.20
Eutectique ternaire	450	3.60	0.36
NaCl–KCl–MgCl$_2$	500	6.08	0.40

de U (IV) dans ce solvant, est suffisante pour provoquer la dismutation ; ce phénomène n'apparaît dans aucun des autres solvants étudiés.

Influence de la température

Pour chacun des solvants étudiés, ainsi qu'il ressort des Figs. 3 à 6, une augmentation de température se traduit par la diminution, à pression en HCl donnée, de la valeur de *L*. En d'autres mots, une augmentation de température diminue la dismutation de UO_2(V).

Influence de la composition du solvant

La Fig. 7 représente les courbes log P_{HCl} en fonction de log *L* pour la dismutation de UO_2(V) dans les différents solvants étudiés à 450° (455° dans LiCl–KCl 70–30 % mol.). Il est intéressant de constater qu'en première approximation, la pente des courbes dépend avant tout du domaine de pression en HCl dans lequel se situent les mesures : en-dessous de 40 mm HCl environ, la pente est voisine de $\frac{1}{2}$ (cas de LiCl–CsCl) ; entre 60 et 150 mm HCl, la pente est voisine de $\frac{1}{4}$ (cas de LiCl–KCl) et au-dessus de 200 mm HCl, elle se rapproche de $\frac{1}{6}$ (cas de NaCl–KCl–$MgCl_2$). Ainsi, la forme prépondérante de l'eau en présence (OH^-, H_2O ou H_3O^+) ne dépend que de la pression en acide chlorhydrique. Ce résultat ne doit pas nous surprendre ; on peut, en effet, écrire les réactions chimiques responsables de la dismutation de la façon suivante :

$$2\,UO_2^+ \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,O^{2-}$$

$$2\,O^{2-} + n\,HCl \rightleftharpoons 2\,(H_3O^+, H_2O, OH^-) + n\,Cl^- \quad (n = 6,4,2)$$

Ceci montre que la pente des courbes ne dépend que des secondes réactions, c'est-à-dire finalement de l'équilibre d'autoprotolyse de l'eau, et pour autant que l'on puisse admettre que cet équilibre n'est pas trop influencé par la nature du bain, on peut s'attendre au résultat trouvé.

Par contre, la position des diagrammes log $P = f(\log L)$ dépend de la nature des cations du solvant : pour une même valeur de P_{HCl}, les valeurs de *L* vont dans l'ordre croissant suivant : eutectique NaCl–KCl–$MgCl_2$ (30–20–50) < mélange LiCl–KCl (70–30) < eutectique LiCl–KCl (58–42) < mélange LiCl–CsCl (55–45). Le passage de LiCl–CsCl (55–45) à LiCl–KCl (58–42) revient pratiquement à remplacer Cs par K^+ ; de même, en passant de LiCl–KCl (58–42) à LiCl–KCl (70–30), K^+ est remplacé partiellement par Li^+.

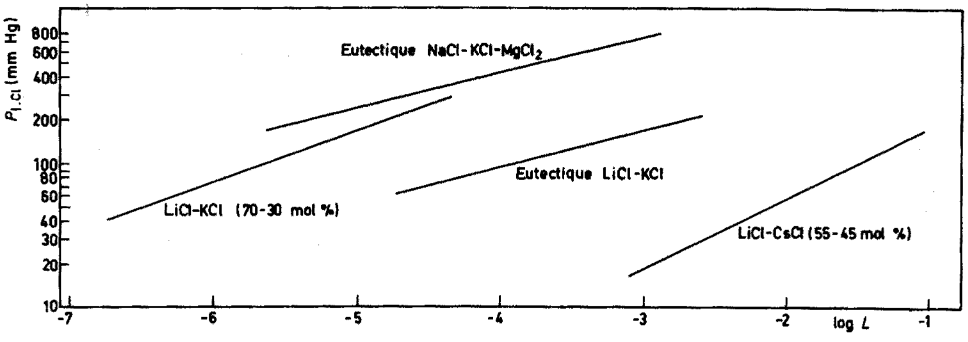

Fig. 7. Comparaison des diagrammes log $P = f$ (log *L*) dans les quatre solvants étudiés à 450°.

Dès lors, le degré de dismutation représenté par la valeur de *L* est précisément l'ordre inverse des densités de charge (rapport charge/surface) des cations du solvant: $Cs^+ < K^+ < Li^+ < Mg^{2+}$. En d'autres mots, plus la densité de charge des cations du solvant est faible (solvant riche en CsCl par exemple), plus l'équilibre de dismutation–amphotérisation est déplacé dans le sens de la formation de U(IV) et UO_2(VI). Ce comportement est à rapprocher de la facilité avec laquelle les ions Cs^+ forment des composés stables avec U(IV) et UO_2(VI) (Cs_2UCl_6 et $Cs_2UO_2Cl_4$). Stromatt[5] montre que la stabilité de UO_2(VI) augmente dans les chlorures alcalins fondus quand diminue la densité de charge des cations du solvant et il attribue ce phénomène à l'augmentation d'activité de chlorure résultant de la diminution de puissance de polarisation des cations du solvant. De même, la tendance de U(IV) à former des complexes octaédriques stables du type UCl_6^{2-} dans les chlorures alcalins fondus augmente quand diminue la densité de charge des cations du solvant[6].

Dans l'eutectique ternaire NaCl–KCl–$MgCl_2$, UO_2(V) jouit d'une stabilité remarquable, se trouvant probablement sous la forme d'un complexe chloré différent de celui existant dans les chlorures alcalins étudiés. Cette stabilité serait responsable du deplacement de l'équilibre dans le sens de l'amphotérisation.

Nous remercions vivement le Fonds National de la Recherche Scientifique et l'Institut Interuniversitaire des Sciences Nucléaires pour l'intérêt constant apporté à nos travaux et le soutien financier accordé à notre laboratoire.

RÉSUMÉ

Les auteurs étudient l'influence de la température (400 à 500°) et de la composition du solvant sur l'équilibre de dismutation–amphotérisation réversible de UO_2(V) en U(IV) et UO_2(VI) dans les chlorures fondus suivants: eutectique LiCl–KCl, LiCl–KCl (70–30 % mol.), LiCl–CsCl (55–45 % mol.) et eutectique NaCl–KCl–$MgCl_2$. L'équilibre est d'autant plus déplacé dans le sens de la formation de UO_2(V) que la température et la densité de charge des cations du solvant sont élevées et que la pression en HCl est faible. Dans le cas de l'eutectique NaCl–KCl–$MgCl_2$ fondu, le déplacement de l'équilibre de dismutation semble dû à la complexation de UO_2(V) par les ions chlorures sous une forme plus stable que dans les chlorures alcalins étudiés.

SUMMARY

The influence of temperature (400–500°), and of the solvent composition on UO_2(V) disproportionation is studied by visible and near infrared absorption spectrophotometry in the following molten chlorides: LiCl–KCl eutectic, LiCl–KCl (70–30 mol %), LiCl–CsCl (55–45 mol %) and NaCl–KCl–$MgCl_2$ ternary eutectic. An increase in temperature or charge density of the cations of the solvent or a decrease in the pressure of HCl, favour the stability of UO_2(V). In the case of molten NaCl–KCl–$MgCl_2$ eutectic, the displacement of the disproportionation equilibrium seems to be due to the complexation of UO_2(V) by chloride ions to form a species more stable than in alkali chlorides.

ZUSAMMENFASSUNG

Der Einfluss von Temperatur (400–500°) und Lösungsmittelzusammensetzung auf die Disproportionierung von UO_2(V) wird in den folgenden geschmolzenen

Chloriden untersucht: LiCl–KCl-Eutektikum, LiCl–KCl (70–30 Mol.%), LiCl–CsCl (55–45 Mol.%) und ternäres NaCl–KCl–$MgCl_2$-Eutektikum. Eine Erhöhung der Temperatur oder der Ladungsdichte der Kationen des Lösungsmittels oder eine Erniedrigung des HCl-Druckes begünstigt die Stabilität von UO_2(V). Die Ursache für die Verschiebung des Disproportionierungsgleichgewichts im Falle von geschmolzenem NaCl–KCl–$MgCl_2$-Eutektikum scheint die Komplexierung von UO_2(V) durch Chlorid zu sein, wobei beständigere Spezies als in Alkalichloriden entstehen.

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DOSAGE OXYDIMETRIQUE EN MILIEU NON AQUEUX DE COMPOSES PHENOLIQUES D'ORIGINE VEGETALE

I. OXYDATION RÉVERSIBLE DE QUELQUES *o*-DIPHÉNOLS

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(Reçu le 5 octobre 1971)

La grande hétérogénéité du groupe des composés phénoliques des tissus végétaux est due au nombre et aux positions variables des radicaux hydroxyles, sur des squelettes carbonés souvent fort différents.

Les composés *o*-diphénoliques peuvent cependant se distinguer des monophénols par leur aptitude à former des quinones en cédant deux électrons. Cette propriété est partagée par les *p*-diphénols mais ces composés sont très peu représentés dans les milieux naturels. Willstätter et Pfannenstiehl[1] obtinrent les premiers des quantités pondérales d'*o*-benzoquinone par oxydation du 1,2-benzènediol à l'aide de l'oxyde d'argent dans l'éther éthylique. Le dosage classique des composés phénoliques par le permanganate[2] est basé sur ces propriétés et, selon Bate-Smith[3] seuls réagiraient les *o*- et *p*-diphénols, mais Monties[4] a récemment montré que les *m*-diphénols sont également oxydés, avec ouverture du cycle benzénique. Outre ce manque de spécificité, les résultats obtenus à l'aide de cette méthode sont généralement approchés car, en milieu aqueux, l'oxydation ne s'arrête pas à un stade défini; des réactions secondaires irréversibles ont lieu, à des vitesses non négligeables, à partir du stade quinonique[5,6]. Par ailleurs, dans un cas aussi simple que la titration permanganique du 1,2-benzènediol, la forme de la courbe potentiomètrique enregistrée dépend, pour un pH déterminé, de la nature du tampon utilisé[4].

Dans ce travail nous avons précisé les conditions expérimentales qui permettent l'oxydation réversible de la fonction *o*-diphénol des composés naturels.

PRINCIPE

L'obtention d'*o*-quinones à partir des *o*-diphénols correspondants semble subordonnée à deux conditions:

(*a*) l'utilisation comme oxydant d'un accepteur d'électrons de force moyenne qui permette d'obtenir l'*o*-quinone sans provoquer la rupture ultérieure du cycle benzénique.

(*b*) le choix d'un milieu dans lequel les quinones formées soient stables.

Dans l'acétonitrile, les ions cuivre(II) ou fer(III) sont des accepteurs d'électrons pour un certain nombre de composés comme les iodures[7,8], la thiourée et l'hydroquinone[9]. Nous avons utilisé ces propriétés pour oxyder les *o*-diphénols. En introduisant un sel cuivrique dans une solution de 1,2-benzènediol dans l'acétonitrile, on constate l'apparation instantanée d'une coloration jaune qui reste stable. L'action d'un agent réducteur, comme l'acide ascorbique, fait disparaître immédiatement cette coloration. Dans les mêmes conditions, le phénol et le *m*-triphénol ne sont pas oxydés, mais la réaction est positive avec le *p*-diphénol et l'*o*-diphénol. Il apparaît donc bien *que seuls les phénols susceptibles de former des quinones sont oxydés.*

Au cours de cette oxydation, le transfert d'électrons fait varier le potentiel du milieu ; nous avons défini des conditions expérimentales qui permettent, par potentiométrie, de mesurer cette variation de manière reproductible. Avec une concentration de 25% d'acide méthanoïque dans l'acétonitrile, les équilibres sont rapidement atteints, les formes quinoniques sont stables et les ions cuivre(I) issus de la réaction ne sont pas oxydés par l'oxygène atmosphérique. L'étude de l'influence, sur ces réactions, des différentes bases associées au cation cuivre(II), nous a fait choisir l'ion acétate. On prépare facilement une solution 0.1 *M* d'acétate de cuivre dans l'acide propanoïque.

MATÉRIEL ET MÉTHODES

Dans cette étude, la spectrophotométrie a été utilisée conjointement à la potentiométrie, pour contrôler le dosage des *o*-diphénols par les ions cuivre(II). Une solution décimolaire de chaque phénol à doser est préparée dans le méthanol absolu. Dans le cas de l'acide chlorogénique, par exemple, une prise d'essai de 0.4 ml de cette solution méthanolique est introduite dans 80 ml d'acétonitrile à 25% d'acide méthanoïque; la concentration molaire finale ($5 \cdot 10^{-4}$ *M*) est ainsi compatible avec les mesures spectrophotométriques sous un parcours optique de 0.1 cm. Un montage approprié déjà décrit[10], permet de faire circuler, par l'intermédiaire d'une pompe péristaltique, la solution entre une cellule potentiométrique et une cellule spectrophotométrique de 0.1 cm de parcours optique. Le titrage est effectué à l'aide d'une

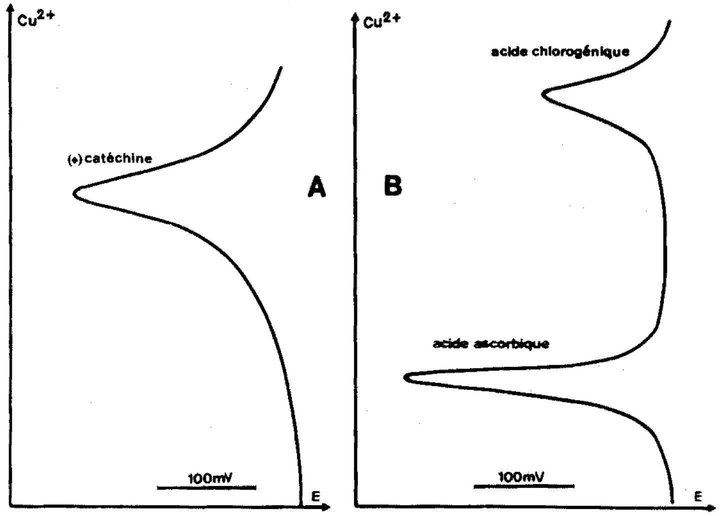


Fig. 1. Courbes différentielles ($\Delta E/\Delta V$) obtenues au cours de l'oxydation par les ions cuivriques de la (+)catéchine (courbe A) et d'un mélange d'acide ascorbique et d'acide chlorogénique (courbe B). Le sommet du pic correspond à la fin de la titration pour chacun des composés.

burette automatique de 1 ml, couplée à l'enregistreur potentiométrique et qui délivre la solution titrante de cuivre(II) en des temps que l'on peut faire varier entre une minute et une heure environ. L'enregistrement potentiométrique est obtenu en utilisant deux électrodes de platine, dont l'une est placée sur le circuit, en amont de la cellule potentiométrique où arrive le réactif. La courbe dérivée résultante (Fig. 1) permet de déterminer facilement la fin de la réaction. Au cours du titrage, l'évolution spectrale est enregistrée entre 250 et 500 nm, à intervalles de temps constants (par exemple 5 min, Fig. 2).

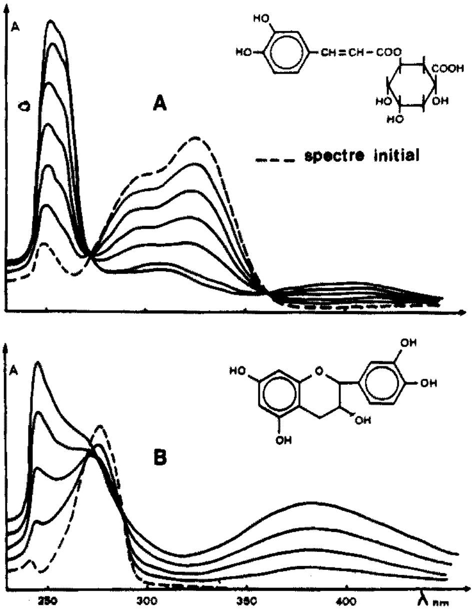


Fig. 2. Evolution des spectres des *o*-diphénols au cours de leur oxydation par les ions cuivriques. (A) Acide chlorogénique; (B) (+)catéchine. Les quinones obtenues sont quantitativement réductibles par l'acide ascorbique, avec retour au spectre initial.

Dans le cadre de ce travail, où nous voulions étudier les phénomènes d'oxydation, la vitesse du titrage était subordonnée d'une part à la vitesse de circulation de la solution entre les deux appareils de mesure et d'autre part au temps nécessaire à l'enregistrement des spectres. Par contre, pour doser seulement un ou plusieurs *o*-diphénols, un simple montage potentiométrique muni d'une électrode platine–calomel peut suffire; il est également possible d'utiliser un indicateur d'oxydoréduction pour marquer la fin du titrage. Dans ces conditions, les dosages ne nécessitent que quelques minutes.

RÉSULTATS ET DISCUSSION

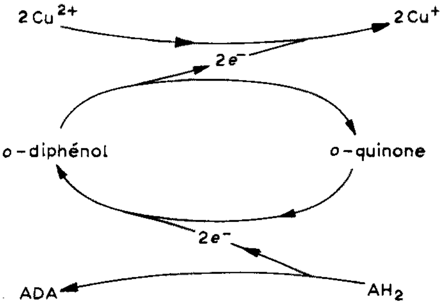
En appliquant les méthodes décrites, nous avons dosé un certain nombre d'*o*-diphénols simples (1,2-benzènediol) ou plus complexes comme les acides caféique, dihydrocaféique, chlorogénique et la (+)catéchine. Ces deux derniers composés ont été retenus pour illustrer ces phénomènes d'oxydation.

Au cours du dosage, l'oxydation de l'acide chlorogénique se traduit spectrophotométriquement par la disparition de la bande d'absorption située à 325 nm (Fig. 2A) avec apparition de deux autres bandes, l'une étroite vers 250 nm et l'autre beaucoup plus large vers 392 nm, responsable de la couleur jaune.

La forme quinonique obtenue lors du dosage de la (+)catéchine présente un maximum d'absorption à 380 nm (Fig. 2B). Cette forme est stable, à condition qu'il n'y ait pas d'ions cuivre(II) en excès dans le milieu. En effet, dans ce dernier cas, on observe une augmentation lente et irréversible de l'absorption à 380 nm. Ce phénomène correspond probablement à une réaction du type *o*-quinone $\xrightarrow{-e^-}$ polymères qui est classique en milieu aqueux.

Dans tous les cas, les quinones formées sont réductibles par l'acide ascorbique (AH_2) avec formation d'acide déhydroascorbique (ADA), cette réduction intervenant après celle des ions cuivre(II) éventuellement en excès dans le milieu.

Ces phénomènes peuvent être schématisés par l'équation:



Les composés naturels ne possédant pas de fonction *o*-diphénol comme la phloridezine, le phloroglucinol, l'apigénine et la naringénine ne sont pas oxydables par les ions cuivre(II) dans les conditions expérimentales définies. Par contre, les diénols comme l'acide ascorbique sont quantitativement oxydés avec échange de deux électrons par molécule, mais le potentiel de ces couples oxydo-réducteurs est tel que l'oxydation intervient avant celle des *o*-diphénols. Il est donc éventuellement possible de titrer, par les ions cuivre(II), un mélange d'acide ascorbique et d'un *o*-diphénol en solution; on obtient deux courbes potentiométriques successives (Fig. 1B). Le phénomène peut également être suivi par spectrophotométrie.

Les propriétés oxydantes des ions cuivriques en milieu anhydre, qui permettent d'obtenir facilement des quinones stables à partir des phénols correspondants, sont donc particulièrement intéressantes pour le dosage des composés *o*-diphénoliques des végétaux.

RÉSUMÉ

Certains *o*-diphénols des végétaux (acide chlorogénique, acide caféique, catéchines) peuvent être oxydés par les ions cuivriques, dans un mélange d'acétonitrile et d'acide méthanoïque. L'étude spectrophotométrique et potentiométrique de ces phénomènes montre que les réactions s'effectuent avec un transfert de deux charges électroniques par fonction *o*-diphénol oxydée. Les *o*-quinones obtenues sont stoechiométriquement réductibles par l'acide ascorbique.

SUMMARY

Some *o*-diphenols of plant origin (chlorogenic acid, caffeic acid, catechines) can be oxidized by copper(II) ions, in a mixture of acetonitrile and methanoic acid. A spectrophotometric and potentiometric study of these phenomena shows that the reactions take place with a transfer of two electrons for each oxidized *o*-diphenol function. The *o*-quinones obtained are stoichiometrically reducible by ascorbic acid.

ZUSAMMENFASSUNG

Einige *o*-Diphenole pflanzlicher Herkunft (Chlorogensäure, Kaffeesäure, Catechine) können durch Kupfer(II)-Ionen in einer Mischung von Acetonitril und Ameisensäure oxydiert werden. Die spektrophotometrische und potentiometrische Untersuchung dieser Prozesse zeigt, dass die Reaktionen mit einem Übergang von zwei Elektronen für jede oxydierte *o*-diphenolische Funktion ablaufen. Die erhaltenen *o*-Chinone sind durch Ascorbinsäure stöchiometrisch reduzierbar.

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DOSAGE OXYDIMETRIQUE EN MILIEU NON AQUEUX DE COMPOSES PHENOLIQUES D'ORIGINE VEGETALE

II. OXYDATION DES FLAVONOLS

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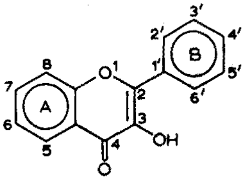
(Reçu le 5 octobre 1971)

La caractérisation et le dosage des flavonoïdes sont essentiellement basés sur l'interprétation des modifications spectrales résultant de la chélation de différents métaux par ces composés[1,2]. Ces réactions nécessitent généralement un grand excès d'ions métalliques, ce qui ne permet pas l'application des méthodes titrimétriques classiques.

Dans l'étude précédente[3], nous avons montré qu'il est possible de doser stoechiométriquement divers composés *o*-diphénoliques comme l'acide chlorogénique et la (+)catéchine en utilisant les propriétés oxydantes des ions cuivriques en milieu non aqueux. Ces principes ont été appliqués dans le présent travail au dosage titrimétrique de quelques flavonols (I) fréquemment rencontrés dans les tissus végétaux.



(I) Structure générale des flavonols

MATÉRIEL ET MÉTHODES

Selon les techniques déjà décrites[3], l'oxydation des flavonols par le cuivre(II) est effectuée dans un milieu acétonitrile–acide méthanoïque, les phénomènes étant suivis simultanément par potentiométrie et par spectrophotométrie. La réversibilité éventuelle des réactions est étudiée par action de l'acide ascorbique sur les produits d'oxydation. Tous les essais ont été effectués à partir de produits Fluka solubilisés dans du méthanol absolu.

RÉSULTATS

Nous avons tout d'abord étudié l'oxydation par le cuivre(II) des flavonols di- ou trihydroxylés en *ortho* sur le cycle B (quercétine, fisétine, myricétine) ainsi que celle de plusieurs de leurs hétérosides en position 3. La mise en évidence du caractère réducteur des flavonols non hydroxylés sur le cycle B (kaempférol) et de quelques flavonoïdes de structure voisine nous a permis ensuite de mieux interpréter les phénomènes observés.

Oxydation des flavonols présentant au moins une fonction o-diphénol sur le cycle B

L'enregistrement potentiométrique réalisé au cours de l'oxydation de la quercétine (5, 7, 3′, 4′-tétrahydroxyflavonol) présente deux pics ; le premier correspond à deux équivalents de cuivre par molécule et le second à une consommation supplémentaire de 0.75 équivalent (Fig. 1A). L'évolution spectrale au cours de l'oxydation traduit la disparition des bandes d'absorption vers 260 et 370 nm et l'apparition d'une bande nouvelle vers 290 nm (Fig. 2A). Quel que soit le stade d'oxydation de la molécule, la réaction n'est pas réversible. Par contre, dans les mêmes conditions, l'oxydation

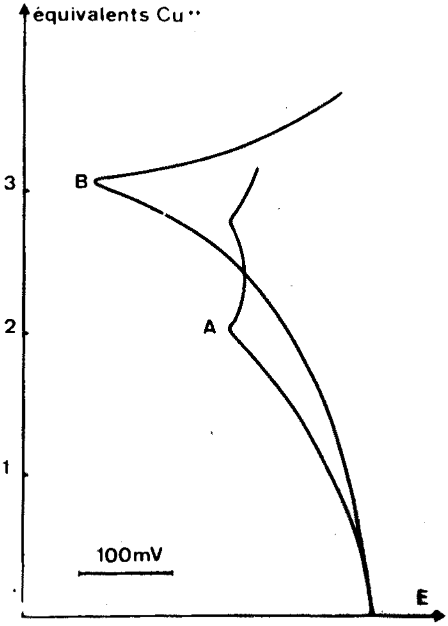


Fig. 1. Courbes potentiométriques obtenues au cours de l'oxydation par le cuivre(II) de la quercétine (A) et de la myricétine (B).

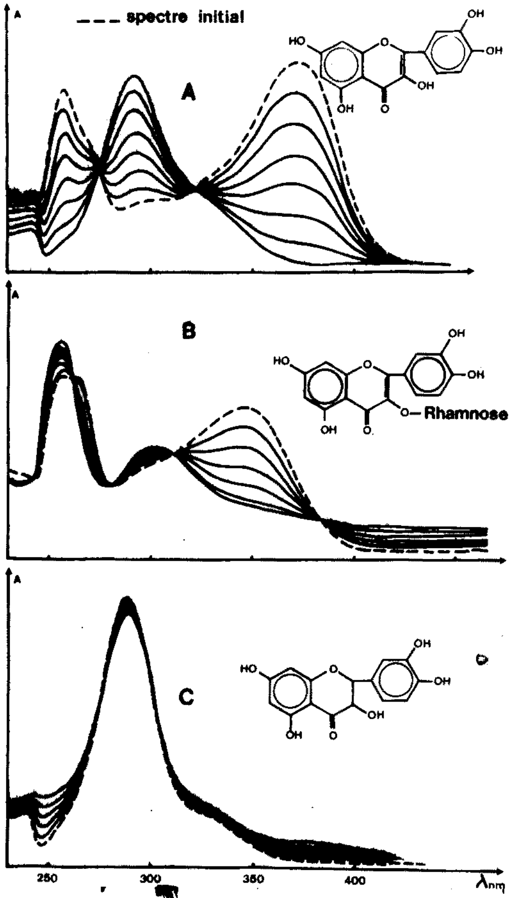


Fig. 2. Evolutions spectrophotométriques au cours de la titration par le cuivre(II) de la quercétine (A), de la quercitrine (B) et de la dihydroquercétine (C). Dans les deux derniers cas, les *o*-quinones formées sont réductibles par l'acide ascorbique avec retour au spectre initial.

de deux hétérosides de la quercétine, la quercitrine (quercétine 3-rhamnoside) (Fig. 2B) et la rutine (quercétine 3-rutinoside), nécessite deux équivalents de cuivre(II) par molécule et est totalement réversible.

Pour mettre en évidence l'influence de l'état d'hydrogénation de l'hétérocycle des flavonols sur leurs propriétés réductrices, nous avons fait agir le cuivre(II) sur un dihydroflavonol, dihydroxylé sur le cycle B: la 2, 3-dihydroquercétine. L'oxydation de ce composé (Fig. 2C) nécessite deux équivalents cuivriques et le phénomène est entièrement réversible. L'oxydation de la fisétine (7, 3', 4'-trihydroxyflavonol) qui est l'homologue non hydroxylé en position 5 de la quercétine, s'effectue en deux étapes: une étape non réversible, correspondant à la consommation d'un équivalent cuivre(II) par molécule et une seconde étape réversible, par action de l'acide ascorbique, correspondant au transfert d'un électron par molécule (Fig. 3).

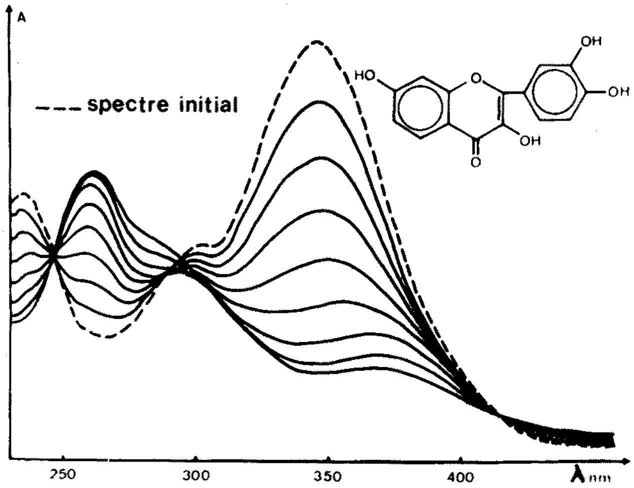


Fig. 3. Evolution spectrophotométrique au cours de la titration de la fisétine par le cuivre(II).

L'oxydation de la myricétine (5, 7, 3', 4', 5'-pentahydroxyflavonol) rapelle celle de la quercétine: l'enregistrement potentiométrique ne montre qu'un seul pic (Fig. 1B) correspondant à la fin de l'évolution spectrale (Fig. 4A) et à la consommation de 3 équivalents de cuivre(II) par molécule; le produit de la réaction n'est par réductible.

Oxydation des flavonols ne présentant pas de fonction o-diphénol sur le cycle B

Bien que ne possédant pas de groupement réducteur sur le cycle B, le kaempférol (5, 7, 4'-trihydroxyflavonol), le kaempféride (5, 7-dihydroxy-4'-methoxyflavonol) et la galangine (5, 7-dihydroxyflavonol) sont oxydés par le cuivre(II) avec une consommation de 1.5 équivalent par molécule. L'évolution spectrophotométrique (Fig. 4B) est semblable à celle observée pour les flavonols dont le cycle B est polyhydroxylé. Cependant, dans le cas de la galangine, l'oxydation est beaucoup plus lente que pour les deux autres composés et, à la température ambiante, la réaction n'est pas assez rapide pour permettre dans ces conditions le dosage volumétrique de cette substance. Un dihétéroside du kaempférol, la robinine (kaempférol 7-rhamnoside 3-galactorhamnoside), n'est pas oxydé par les ions cuivriques et il en est de même pour une flavone

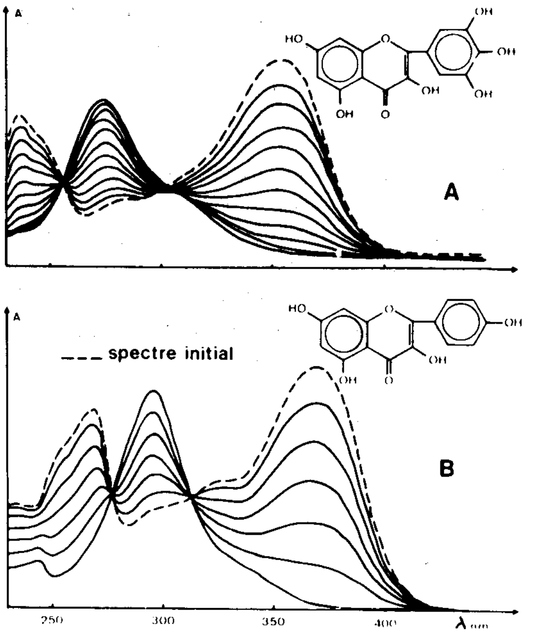


Fig. 4. Evolution spectrophotométrique au cours de la titration, par le cuivre(II), de la myricétine (A) et du kaempférol (B).

monohydroxylée comme le kaempférol sur le cycle B, l'apigénine (5, 7, 4'-trihydroxyflavone).

DISCUSSION

Les résultats précédents font ressortir l'influence de l'état d'oxydation de l'hétérocycle des flavonols ainsi que du degré de substitution des cycles A et B sur le caractère réducteur des molécules.

Importance de l'état d'oxydation de l'hétérocycle

Le kaempférol est facilement et irréversiblement oxydé par le cuivre(II) avec transfer de deux électrons pour trois molécules. Par contre, les 3-hétérosides de ce corps (robinine) ou son homologue non hydroxylé en 3 (apigénine) ne le sont pas. La présence de la fonction hydroxyle libre, sur l'hétérocycle oxygéné, confère donc un caractère réducteur certain à la molécule flavonolique et cette propriété est indépendante de l'existence éventuelle d'une fonction *o*-diphénol sur le cycle B. La stoechiométrie des réactions d'oxydation implique au moins une dimérisation de la molécule dans le cas du kaempférol ou une tétramérisation, notamment lors du second stade d'oxydation de la quercétine. Cela pourrait expliquer l'irréversibilité des réactions. Les transformations spectrales enregistrées au cours de l'oxydation de la quercétine (Fig. 2A), de la fisetine (Fig. 3), de la myricetine (Fig. 4A) et du kaempférol (Fig. 4B) traduisent la disparition des effets de conjugaison du groupement CO de l'hétérocycle avec le cycle B (bande vers 370 nm) et avec le cycle A (bande vers 260 nm) signalés par Geissman[4] et Jurd[5]. Lorsque les effets tautomères de la molécule sont supprimés par blocage de l'hydroxyle en position 3 (quercitrine) ou par hydrogénation de la double liaison en 2, 3 (dihydroquercétine), la fonction *o*-diphénol du cycle B est alors normalement oxydable en *o*-quinone, avec apparition d'une bande d'absorption d'intensité plus faible entre 400 et 450 nm (Fig. 2B et C). Ces *o*-quinones sont réductibles par l'acide ascorbique. La comparaison des spectres de la quercétine et de la dihydroquercétine (Fig. 2A et 2C) met d'ailleurs en évidence la disparition du caractère aromatique de l'hétérocycle dans le cas du second composé.

Influence de l'état d'hydroxylation du cycle A

La comparaison des résultats, obtenus d'une part avec la quercétine et d'autre part avec la fisétine, indique que l'hydroxyle en position 5 sur le cycle A active l'hétérocycle au détriment du pouvoir réducteur de la fonction *o*-diphénol du cycle B. En effet, l'oxydation est totalement irréversible pour la quercétine, alors qu'elle l'est partiellement dans le cas de la fisétine. Pour ce dernier composé, après un stade irréversible, lié vraisemblablement à la formation d'un dimère, on observe un second stade réversible, ce qui implique sur le dimère l'existence d'une seule fonction *o*-diphénol active. L'influence éventuelle de l'hydroxyle en position 7 reste à préciser.

Influence de l'état d'hydroxylation du cycle B

L'effet activateur des hydroxyles du cycle B est mis en évidence lorsque l'on compare les résultats obtenus en oxydant le kaempférol, le kaempféride et la galangine, ce dernier composé se révélant nettement moins réducteur que les deux autres. Lorsque le cycle B des flavonols est dihydroxylé (quercétine) ou trihydroxylé (myricétine), les fonctions phénoliques de ce cycle semblent intervenir davantage par leur effet activateur sur l'hétérocycle que par leur pouvoir réducteur propre. Ceci expliquerait le fait que ces composés ne donnent pas de formes quinoniques lors de l'oxydation. Ces phénomènes sont mis en évidence par la similitude des évolutions spectrophotométriques du kaempférol et de la myricétine. Dans ces deux cas, les effets optiques, sensiblement les mêmes, sont davantage liés au caractère aromatique particulier de l'hétérocycle qu'au degré de substitution du cycle B. Il faut cependant noter que l'oxydation de la myricétine et de la quercétine conduit à la formation immédiate de dérivés quinoniques intermédiaires de coloration rouge, qui disparaissent au fur et à mesure de leur formation. Une réaction plus lente conduit ensuite aux formes oxydées finales, stables et non réductibles.

CONCLUSION

Le type de réaction réversible précédemment étudié[3] lors de l'oxydation de certains *o*-diphénols, ne peut pas être généralisé à l'ensemble des composés naturels présentant cette structure. En effet, indépendamment de l'existence de fonctions *o*-diphénol sur le cycle B, les flavonols présentent un caractère réducteur particulier dû à la structure caractéristique de leur hétérocycle.

L'utilisation de ces propriétés permet de doser volumétriquement un flavonol déterminé, par une solution titrée de cuivre(II) dans l'acide propanoïque. Il suffit, pour cela, de déterminer au préalable la stoechiométrie de la réaction, stoechiométrie qui varie avec l'état d'hydroxylation des cycles A et B du flavonol considéré. La non réversibilité de la réaction d'oxydation de la plupart des flavonols, peut être utilisée, si ces composés sont en présence d'autres polyphénols, dont les produits d'oxydation sont réductibles par l'acide ascorbique. L'application de ces principes aux extraits végétaux, nous a permis de doser sélectivement certains polyphénols, en exploitant les modifications spectrales résultant de l'oxydation de ces composés par le cuivre(II).

RÉSUMÉ

Dans un milieu anhydre, il est possible de doser volumétriquement les flavonols en les oxydant par les ions cuivriques. Dans ces conditions, les fonctions *o*-diphénol éventuellement présentes sur le cycle B ne montrent plus de caractère réducteur spécifique. L'hydroxylation des cycles A et B en positions 5 et 4′ augmente, par activation de l'hétérocycle, le caractère réducteur de la molécule. Ces phénomènes n'ont plus lieu lorsque l'hydroxyle, en position 3 sur l'hétérocycle, est lié à un glucide ou lorsque cet hétérocycle est hydrogéné en positions 2 et 3. Par contre, dans ces conditions, si le cycle B est porteur d'une fonction *o*-diphénol, on peut obtenir l'*o*-quinone correspondante, quantitativement réductible par l'acide ascorbique.

SUMMARY

Flavonols can be titrated in non-aqueous medium by oxidation with copper(II) ions. Under these conditions, possible *o*-diphenolic functions present on ring B no longer show specific reducing character. Hydroxylation of rings A and B, in the 5 and 4′ positions, increases the reducing character of the molecule by activation of the heterocycle. These phenomena do not occur when the hydroxyl group in position 3 on the heterocycle is glucosided, or when the heterocycle is hydrogenated in positions 2 and 3. However, under these conditions, if ring B bears an *o*-phenolic function, one can obtain the corresponding *o*-quinone, which is quantitatively reducible by ascorbic acid.

ZUSAMMENFASSUNG

Flavonole können in wasserfreiem Medium mit Kupfer(II)-Ionen oxydimetrisch titriert werden. Unter diesen Bedingungen zeigen die am Ring B möglicherweise vorhandenen *o*-diphenolischen Funktionen keinen spezifischen Reduktionscharakter mehr. Die Hydroxylierung der Ringe A und B in Stelle 5 und 4′ steigert durch Aktivierung des Heteroringes die reduzierenden Eigenschaften des Moleküls. Dies trifft nicht mehr zu, wenn die Hydroxylgruppe in Stelle 3 am Heteroring glukosidiert wird oder wenn dieser Heteroring in Stelle 2 und 3 hydriert wird. Jedoch kann man unter diesen Bedingungen, wenn der Ring B eine *o*-diphenolische Funktion aufweist, das entsprechende *o*-Chinon erhalten, das durch Ascorbinsäure quantitativ reduzierbar ist.

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INTERMEDIATE STORAGE TECHNIQUE IN ORGANIC MICROANALYSIS

PART I. DETERMINATION OF HALOGENS

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During the past years relatively few papers have been published concerning halogen determinations by tube combustion. This is probably due to the worldwide use of the Schöniger flask combustion technique[1]. However, the flask combustion method is not always suitable for liquid, volatile, or metal-containing compounds, and it is necessary to have an alternative method available. The one most similar technically to the standard methods for carbon, hydrogen, nitrogen and oxygen, is the tube combustion procedure. It should, therefore, be preferred to the Carius or fusion techniques, obviously not in the classical catalytic combustion modification, but with an empty tube at relatively high temperatures and oxygen flow rates with some arrangement to produce turbulent flow conditions, as in the method of Belcher and Ingram[2].

As the many publications (*e.g.* Belcher and Fildes[3]) on empty-tube determinations of halogens have proven, it is quite difficult to ensure complete absorption of the halogens from rapid gas streams. Strongly alkaline media and/or elaborate absorption vessels with frits, necessitating thorough rinsing, are required. Moreover, as the halogens leave the combustion tube as a mixture of HCl and Cl_2, HBr and Br_2, and I_2 and I_2O_5, respectively, together with oxides of nitrogen and all other combustion products, the alkaline absorbing liquid must also have reducing properties. This, together with the large volume of rinsings, reduces the choice of methods for the final determination. No reducing reagents in the absorbing liquid would be necessary and the ease of dissolution of the gaseous products would be increased, if the combustion products could be reduced within the combustion tube. This has been attempted by Kirsten[4] but the method seems to have gained no popularity. This is undoubtedly due to the rather complicated apparatus, the potential danger of the simultaneous presence of oxygen and hydrogen in the hot combustion tube, and the possible side-reactions between hydrogen and other combustion products. In the present work, experiments with such an apparatus indicated that this method gave usable results only under strictly controlled conditions of gas flow and combustion speed and if a G3 frit was used in the absorption vessel. Otherwise, white fumes appeared and the results were low.

It was therefore decided to perform sample oxidation and halogen reduction as two separate steps. The sample is oxidized in a rapid flow of oxygen and the halogens

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are absorbed on metallic silver. During the sweeping period with nitrogen, which is necessary to remove all oxygen, the halogens are stored on the silver. The time of this storage can be optionally prolonged to any length. Thereafter, the silver halides are reduced with a slow flow of hydrogen and the hydrogen halides are easily absorbed in a small volume of distilled water in a simple flask. Thus all methods of final determination can be used, even alkalimetric titration, for all other combustion products leave the combustion tube during the oxidation step.

The oxidation of organic compounds and the absorption of halogens with silver have been thoroughly described in the literature, but not the reduction of silver halide,

$$2\,AgX + H_2 = 2\,Ag + 2\,HX \qquad (1)$$

Thermodynamic calculations showed, as might be expected, that silver chloride is reduced most easily, followed by silver bromide and iodide[5]. The equilibrium is, as can be seen from Table I, always on the side of the silver salt. However, as the hydrogen passes over the solid, even a quite small equilibrium concentration of hydrogen halide is sufficient and quantitative reduction is achieved in a short time. Figures 1, 2, and 3 show the relation between time and reaction rate at various temperatures. It can be seen that the reaction of silver chloride at low temperatures is much slower than would be expected from the equilibrium constants. Probably the diffusion process within the crystal lattice is too slow at those temperature. Therefore it is best to use one standard temperature, 480°, which is well within the range of temperatures recommended for halogen absorption[7].

TABLE I

REDUCTION OF SILVER HALIDES

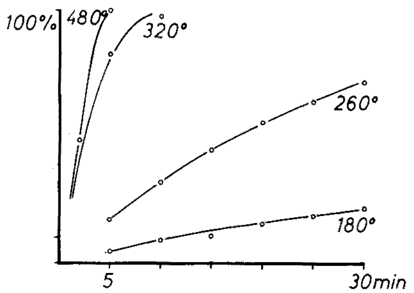
$$AgX + \tfrac{1}{2}H_2 \rightleftarrows Ag + HX;\; K = \frac{[HX]}{[H_2]^{\frac{1}{2}}}$$

T (°K)	$X = Cl$		$X = Br$		$X = I$	
	log K^a	t_{th}^b	log K	t_{th}	log K	t_{th}
453	−0.51	< 0.1	−3.76	60	−6.77	31000
533	−0.12	< 0.1	−2.70	5.3	−5.27	1200
593	0.38	< 0.1	−2.10	1.3	−4.42	170
753	0.96	< 0.1	−1.00	0.1	−2.83	4.5
893	1.28	< 0.1	−0.38	<0.1	−1.94	0.6

[a] The log K values were calculated by the second approximation formula of Ulich[6].

[b] t_{th} is the time in minutes needed for a hydrogen flow of 30 ml min^{-1} to sweep 1 mg of halogen out of the silver layer if the equilibrium is established instantaneously.

The resulting hydrogen halides can be fed through a tubing of virtually any length without loss (up to 10 m have been employed), provided that the tubing is dry and not hygroscopic, preferably made of polyethylene or Teflon. In such tubing and at the high gas flow used, any water formed by combustion will not condense, even if compounds with 10% hydrogen content are burned[8]. If there is only a trace of



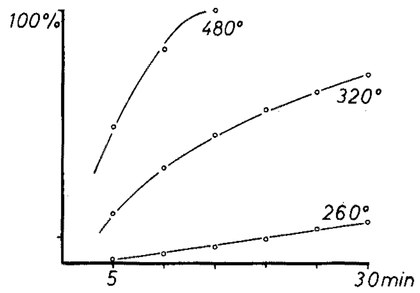


Fig. 1. Elution rate of chlorine (2 mg) *vs.* time at various temperatures.

Fig. 2. Elution rate of bromine (2 mg) *vs.* time at various temperatures.

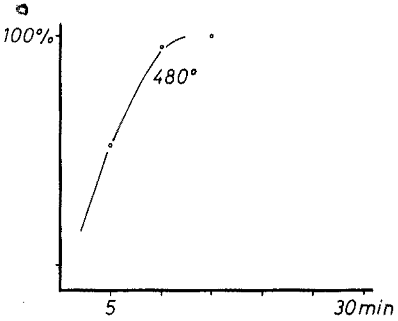


Fig. 3. Elution rate of iodine (2 mg) *vs.* time.

water within the tubing, white fumes which cannot be absorbed, would form during the passage of the hydrogen halide.

EXPERIMENTAL

Apparatus

Care was taken to keep the number of custom-made parts to a minimum and to use commercially available items wherever possible. The furnace used was a Heraeus Micro U combustion unit, with a main furnace of 200 mm length. The additional silver oven was a 60-mm long transparent quartz burner (P. Haack, A-1090 Wien). Its temperature was set with a variable transformer and controlled with a thermocouple. Oxygen, nitrogen, and hydrogen were fed through copper lines to solenoid valves (solenoid valves 133 A 04, Lucifer Ltd., CH-8610 Uster); the arrangement is shown in Fig. 4. One flowmeter with needle valve was used for all gases (Type DK 27N, 0.6–6 l air h^{-1}, L. Krohne, D41 Duisburg), the different flow rates being adjusted by the pressures from the reducing valves. The coil of the first solenoid valve was connected in parallel to the driving motor for the movable furnace; it was energized and the oxygen flow opened as long as the furnace travelled, and then it switched to nitrogen. After the time necessary to replace all oxygen in the tube with nitrogen, the second valve was energized manually, opening for hydrogen and closing the flow from the first valve. All gases were purified by passing through a layer of soda asbestos between the flowmeter and the combustion tube.

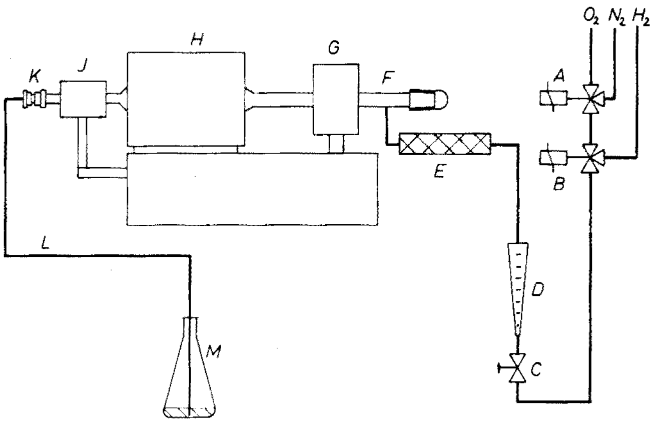


Fig. 4. Diagram of the apparatus. (A) Solenoid valve 1; (B) solenoid valve 2; (C) needle valve; (D) flowmeter; (E) purification tube; (F) combustion tube; (G) movable burner; (H) main furnace; (J) silver oven; (K) connector; (L) polyethylene tubing; (M) absorbing flask.

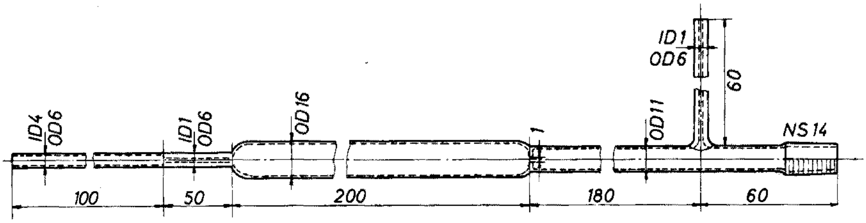


Fig. 5. Combustion tube.

The combustion tube was made of quartz to the dimensions given in Fig. 5. The constriction at the beginning of the wide part caused the flow to become turbulent, enabling the combustion of samples up to 15 mg within 4 min without formation of soot. Of course, other constructions can be used, provided that their oxidation capacity is sufficient. Care must be taken that no cold zone exists between the main combustion furnace and the silver oven, in order to avoid condensation. The connecting part of the tube should be of thick-walled capillary tubing to improve the thermal conductivity. The connector at the end of the combustion tube has a Teflon body and is tightened with Viton 0-rings (MF-Kupplung DE, Serva Technik, D6909 Malsch).

The absorption vessel was a simple 100-ml Erlenmeyer flask, with a ground-glass stopper if an iodimetric finish was to be used. A piece of polyethylene tubing (1 mm i.d.) was attached to the connector and its end was dipped into the water in the flask. No stirring or shaking was necessary for quantitative absorption.

Reagents

Silver wool, as for the determination of carbon and hydrogen.

Solutions and indicators for the determination of chloride, bromide, and iodide, by any standard method. In the present work, titration with mercury(II) perchlorate in 80% ethanol in presence of diphenylcarbazone as indicator[9] was preferred for chloride and bromide, and titration with sodium thiosulfate after oxidation with bromine[10] for the determination of iodine.

Procedure

The quartz tube was washed and dried, and a layer of silver wool, *ca.* 5 mm long was introduced into the narrow end of the tube and pushed firmly to the constriction. The tube was mounted, all connections were made and the furnaces were heated to their optimal temperatures (950° for the main burner, 850° for the movable burner, and 480° for the silver oven). The gas pressures were adjusted to produce by a standard setting of the needle valve, flows of 50 ml min^{-1} for oxygen and nitrogen, and 30 ml min^{-1} for hydrogen. Care should be taken to correct the hydrogen reading as the flowmeter is calibrated for air.

A sample of 1–10 mg, depending on the halogen content, was weighed in a platinum boat. If the sample was expected to contain inorganic constituents, it was covered with vanadium pentoxide. The boat was placed into the tube, 40–50 mm before the long burner, and the ground-glass cap was secured in position with a spring-clip. The movable burner was placed over the tube and the combustion was

TABLE II

RESULTS OBTAINED FOR STANDARD COMPOUNDS

Compound	*% Halogen*		*Deviation (%)*
	Found	*Calculated*	
p-Chlorobenzoic	22.54	22.65	−0.11
acid	22.74		+0.09
	22.42		−0.23
	22.79		+0.14
	22.49		−0.16
	22.44		−0.21
	22.75		+0.10
	22.77		+0.12
	22.88		+0.23
1-Chloro-2,4-dinitrobenzene	17.45	17.50	−0.05
	17.26		−0.24
	17.59		+0.09
S-Benzylthiuronium	17.44	17.49	−0.05
chloride	17.65		+0.16
Potassium chloride	47.67	47.56	+0.11
$+V_2O_5$	47.71		+0.15
p-Bromobenzoic acid	39.53	39.75	−0.22
	39.72		−0.03
	39.76		+0.01
	40.00		+0.25
o-Bromonitrobenzene	39.36	39.56	−0.20
	39.63		+0.07
o-Iodobenzoic	50.91	51.17	−0.26
acid	51.04		−0.13
p-Iodonitrobenzene	51.19	50.96	+0.23
	51.10		+0.14

performed within 4 min in a stream of oxygen. When the movable burner stopped, the solenoid valve switched to nitrogen. Two minutes later, the movable burner was removed and the second solenoid valve was energized to start the hydrogen flow. The reduction time depended on the halogen present; for chlorine 5 min, for bromine 10 min, and for iodine 15 min were necessary. Thereafter, a further 2 min of nitrogen flow was used to remove all hydrogen from the tube and to transfer the last traces of hydrogen halide to the absorption flask. This flask was charged with 5 ml of distilled water and the exit tubing was immersed into it when the hydrogen flow started. A few drops of hydrogen peroxide were added in the case of sulfur-containing compounds to oxidize the sulfur dioxide which is produced under the conditions of the halogen determination. As has already been mentioned, the final determination can be made by any standard technique, as there are no foreign ions that might interfere. The blank is usually zero.

RESULTS AND DISCUSSION

Test samples analyzed by this method gave the results summarized in Table II. Large numbers of samples have also been analysed under routine conditions with good results.

It is intended to apply the principle of intermediate storage to the determination of sulfur, and to simultaneous determinations of several elements and trace analysis. Further papers will be published on those subjects.

SUMMARY

A method is described for the microdetermination of halogens in organic compounds. The samples are burned in a rapid flow of oxygen (50 ml min^{-1}) at 950° and the halogens are stored in a heated silver layer at 480°. After the combustion the silver halides are reduced with hydrogen (30 ml min^{-1}) and the hydrogen halides are easily absorbed in a small quantity of water. As the solution contains no foreign ions, any procedure for completing the determination can be used.

RÉSUMÉ

On décrit une méthode pour le microdosage des halogènes dans les composés organiques. Les échantillons sont brûlés dans un rapide courant d'oxygène (50 ml min^{-1}) à 950°; les halogènes sont recueillis sur couche d'argent, chauffée à 480°. Après combustion les halogénures d'argent sont réduits par l'hydrogène. Les composés hydrogénés sont ensuite facilement absorbés dans l'eau, et dosés par volumétrie.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur Mikrobestimmung von Halogen in organischen Verbindungen beschrieben. Die Probe wird dabei im raschen Sauerstoffstrom verbrannt und das Halogen in einer erhitzten Silberschicht gespeichert. Nach beendeter Verbrennung wird das Silberhalogenid durch einen langsamen Wasserstoffstrom reduziert und die Halogenwasserstoffe können leicht in einem kleinen Volumen

Wasser absorbiert werden. Da die Lösung keine anderen Ionen enthält, kann jede massanalytische Endbestimmung verwendet werden.

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THE PYROHYDROLYTIC DETERMINATION OF FLUORIDE

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Since Warf *et al.*[1] first introduced the technique several authors[2-16] have reported on the use of pyrohydrolysis to determine the fluoride content of various inorganic materials, but only the reaction conditions seem to differ to a large extent.

The platinum reactor tube in Warf's apparatus[1,3-6] has been replaced by nickel[2,8,9], quartz[7,10,11,13-17] and ceramic[12].

In general, pyrohydrolysis has been carried out in the presence of a reactive oxide. Recommended are: triuranium octaoxide[1,6,7,9], alumina[3,8], silica[8,12,13], vanadium pentoxide[8,9,14,15], tungstic trioxide[7,11,12]; the most striking feature is probably the use of tungstic trioxide[7,11]. Some authors have used a flux, such as a mixture of sodium tungstate and tungstic trioxide[17] or a melt of bismuth trioxide, vanadium pentoxide and sodium tungstate[16].

Generally the reaction is carried out by passing superheated steam[1-6,8-10,14] over the reaction mixture at temperatures between 800 and 1200°. In some cases[7,11-13,15-17], superheated steam is replaced by moist oxygen or moist air.

In the present paper, a pyrohydrolytic method suitable for rapid routine analyses is described. Some reactive oxides and fluxes are compared, as are different carrier gases. The final procedure is based on reaction with superheated steam in a nitrogen stream at 800–1000°, the sample being mixed with sodium ditungstate or lithium ditungstate.

EXPERIMENTAL

Apparatus

The pyrohydrolysis apparatus used (Fig. 1) consists of the following parts.

Nitrogen gas cylinder with regulators and flowmeter.

Steam generator (Büchi).

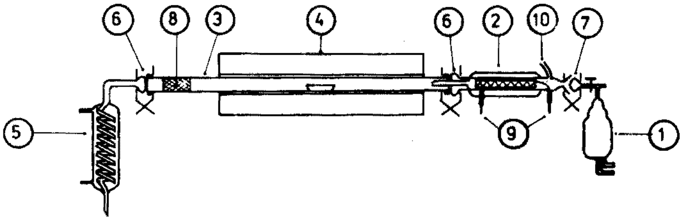

Fig. 1. Apparatus for fluoride determination by pyrohydrolysis. (1) Steam generator, (2) superheater, (3) reactor tube, (4) furnace, (5) coil condenser, (6) Quickfit clamp, (7) Quickfit clamp, (8) quartz wool, (9) supply wires, (10) nitrogen inlet.

Quartz superheater with the outer mantle evacuated. Platinum wire, length 600 mm and diameter 0.5 mm, is used as the heating element. The platinum supply wires are 1.5 mm in diameter and are connected to the 9 V terminals of a soldering transformer, primary 220 V, secondary 9 V, 13.2 A.

Gas-tight alundum reactor tube (Koppers T.E.), length 600 mm, outer diameter 30 mm and inner diameter 23 mm. Cemented ceramic cuffs are attached to the outer ends of the tube, while the ends are ground on the inside to match the ground quartz ball-shaped joints of superheater and condenser.

Electric tube furnace 220 V 2 kW, length 420 mm, inner diameter of tube 40 mm. Maximum temperature 1200°. Temperature is controlled with the aid of a variable transformer (220 V 2080 VA).

Quartz coil condenser: length of coil 1500 mm, outer diameter of coil 6 mm and inner diameter 4 mm.

Platinum boat: length 60 mm, width 10 mm, height 10 mm.

A 400-ml polyethylene beaker.

Quickfit clamps (J.C. 3/35) are modified to suit the connection of the condenser and reactor tube to, respectively, the reactor tube and the superheater.

Reagents

Reagent-quality chemicals and demineralized water were used in the preparation of all reagents and in the procedure followed.

$Na_2W_2O_7$[18]. This is prepared by melting sodium carbonate and tungstic trioxide (molar ratio 1:2) or by melting sodium tungstate and tungstic trioxide (molar ratio 1:1). After cooling, the melt is ground in an agate mortar.

$Li_2W_2O_7$[18]. This is prepared in similar way to sodium ditungstate.

Buffer solution (*pH* 6.5). 80 ml of pyridine is diluted to 900 ml and adjusted to pH 6.5 with hydrochloric acid. The solution is then diluted to 1 l.

Procedure

First cover the bottom of the platinum boat with 1 g of sodium ditungstate. On this weigh a 200-mg sample and then cover with 1 g of sodium ditungstate. By means of a quartz rod push the platinum boat into the reactor tube from the superheater end in such a way that the centre of the platinum boat is at the hottest part in the reactor tube ($1000 \pm 20°$). After this, close the connection between the reactor tube and superheater, using a Quickfit clamp for this purpose. Carry out the pyrohydrolysis for 30 min, while the condensate is collected in a polyethylene beaker. Adjust the flow of nitrogen to 1 l min^{-1} and the flow of superheated steam to 5 g of condensate per min.

In exceptional cases, *e.g.* in analyzing barium fluoride, lithium ditungstate is preferred to sodium ditungstate as the flux.

If no other acids, such as hydrogen chloride and/or hydrogen bromide are liberated by pyrohydrolysis, titrate the solution with standard sodium hydroxide solution and phenolphthalein as the indicator. Since traces of hexafluorosilicic acid are present, first titrate the solution to a persistent colour change; then transfer the solution to a glass beaker, heat to the boiling point, and titrate until the end-point is definitely reached.

In the presence of other acids, titrate the solution potentiometrically with cerium(III) nitrate or lanthanum(III) nitrate solution[20,21] using the lanthanum fluoride membrane electrode for end-point detection. Before titrating, neutralize the solution to pH 6–7 with sodium hydroxide, and, if necessary, concentrate by evaporation. Add the buffer solution (one tenth of the total volume) and make the solution to be titrated up to 50% (v/v) in ethanol. Then titrate potentiometrically with standard cerium(III) or lanthanum(III) solution, using the point of maximal slope as the end-point. Standardize the titrant solution in the same way against a known quantity of fluoride obtained from purified reagent-quality sodium fluoride[19].

DISCUSSION

Choice of auxiliary reagent

As earlier observed by Warf *et al.*[1], fluorides can be distinguished into two groups: a rapidly pyrohydrolyzable group and a slowly pyrohydrolyzable group. The fluorides of the alkaline and alkaline-earth metals belong to the latter group. It should be noted that there are substantial differences in reaction velocity in pyrohydrolyzing, *e.g.* sodium fluoride, precipitated calcium fluoride, mineral calcium fluoride (fluorspar). Indeed, fluorspar can be considered one of the most difficult fluorides to pyrohydrolyze.

The reactivities of tungsten trioxide and of the ditungstates of potassium, sodium and lithium were investigated by subjecting the above-mentioned fluorides to pyrohydrolysis. In this investigation, 900 mg of tungsten trioxide or 2 g of the other reactants were used for every 200 mg of sample. These quantities are about 1.5 times the theoretical amounts needed to conform to the reactions:

$$CaF_2+WO_3+H_2O \rightarrow CaWO_4+2HF$$

and

$$CaF_2+Na_2W_2O_7+H_2O \rightarrow CaWO_4+Na_2WO_4+2HF$$

It is interesting to note that the lithium, sodium and potassium ditungstates not only participate in the reaction but also act as a flux. For this reason priority should be given to the reactants mentioned instead of to tungsten trioxide.

Further investigations showed that preference should be given to the sodium or lithium ditungstate instead of to the potassium salt. Tungsten trioxide is, as expected, the least reactive.

Time and temperature for reaction

The starting point for this investigation was that the pyrohydrolysis of fluorides should be completed within 30 min for routine work. In analyzing sodium fluoride a temperature of 800° was sufficient to achieve a quantitative liberation of fluoride with any of the reactants mentioned within the time limit.

As mentioned before, the alkaline-earth fluorides are less reactive. For instance, at a temperature of 800°, with any of the ditungstates studied as the reactant, only 90% of the total fluoride content in precipitated calcium fluoride could be recovered. With tungsten trioxide as the reactant the recovery was only 50%. With lithium ditungstate as the reactant, at the same temperature, a recovery of 75% of the fluoride content in fluorspar N.B.S. 79 was achieved, while sodium ditungstate gave a maximum recovery of 50%. However, at a temperature of 1000° with sodium ditungstate as the reactant, a recovery of 99.6% of the fluoride content in fluorspar N.B.S. 79 was obtained within 20 min, while in all subsequent analyses the recovery was complete within 30 min*.

Gas and water flow

In pyrohydrolysis the use of a gas is not essential but the flow of superheated steam should be sufficient to provide quantitative recovery. Because the condensate tends to stick to the walls of the coil in the condenser, a flow of nitrogen (1 l min^{-1}) was used to purge the system.

No influence of the carrier gas—air, oxygen and nitrogen were investigated—was observed. In the presence of sulphides, nitrogen is to be preferred to air or oxygen.

The flow of superheated steam was adjusted to produce 5 g of condensate per min. For rapid and quantitative determination 2 g of condensate per min was just sufficient. Smaller amounts are not recommended. If nitrogen is passed through water at 75, 85 and 90°, about 0.5, 1 and 2 g of condensate per min is carried away with the nitrogen gas.

RESULTS

The suitability of the pyrohydrolysis technique discussed was checked on several samples containing fluoride. Analyzed were NaF, CaF_2, MgF_2, SrF_2, BaF_2, N.B.S. 79 fluorspar, opal glass N.B.S. 91, cryolite, halophosphate, etc.

The method gave excellent results. Representative analyses are shown in Table I.

TABLE I

ANALYSIS OF VARIOUS SAMPLES FOR FLUORIDE

Sample	*F found* (%)	*Standard deviation* (%)	*F theor. or reported* (%)
Fluorspar N.B.S. 79[a]	46.10	0.02	46.15[b]
CaF_2 (Mallinckrodt)	47.04	0.02	—[c]
NaF[d]	45.28	0.02	45.23
Opal glass N.B.S. 91	5.84	0.02	5.72

[a] Sieved through B80 mesh.

[b] Reported value for CaF_2 is 94.83%.

[c] A total analysis was done with the following results: Ca, 50.01% ($s=0.06\%$); CO_3, 0.94% ($s=0.004\%$); H_2O, 2.03% ($s=0.03\%$). With the fluoride result reported here, the total result was 100.02%.

[d] Merck reagent-grade sodium fluoride was further purified[19].

SUMMARY

A simple and quantitative pyrohydrolytic determination of fluoride in inorganic materials such as opal glass and fluorspar is described. The sample is heated with sodium ditungstate or lithium ditungstate at 1000° in a ceramic reactor tube in a flow of nitrogen mixed with superheated steam. After cooling, the condensate is

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* Measurement of the temperature distribution in the reactor tube was by means of a thermocouple (Thermocoax, S.A. Sodern, France) the end of which had been fastened to the bottom of a platinum boat.

collected in a polyethylene beaker and the hydrofluoric acid is determined by titrimetric procedures.

RÉSUMÉ

On décrit un dosage simple et pyrohydrolytique des fluorures dans des substances minérales. L'échantillon est chauffé dans un tube réacteur en céramique, à 1000° en présence de ditungstate de sodium ou de ditungstate de lithium, dans un courant d'azote, mélangé à de la vapeur surchauffée. Après refroidissement, le condensat est recueilli dans un bécher de polyéthylène; l'acide fluorhydrique est dosé par titrage.

ZUSAMMENFASSUNG

Es wird eine einfache und quantitative pyrohydrolytische Bestimmung von Fluorid in anorganischen Stoffen wie Opalglas und Flussspat beschrieben. Die Probe wird mit Natriumdiwolframat oder Lithiumdiwolframat in einem keramischen Reaktionsrohr unter Durchleitung eines Gemisches von Stickstoff und überhitztem Wasserdampf auf 1000° erhitzt. Nach dem Abkühlen wird das Kondensat in einem Polyäthylen-Becherglas gesammelt und die Flusssäure titrimetrisch bestimmt.

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SHORT COMMUNICATIONS

A.c. conductivity measurements in isotachophoresis

In electrophoresis several different methods[1] can be used for the detection of zone boundaries. The development of detectors with a high resolving power is of particular importance in the electrophoretic analysis of proteins, in which many narrow zones are involved. In this field u.v. detection[2] has proved to be superior to other methods, its resolving power being a factor of 10 better than that of the thermometric method[3,4].

In the present communication, a method based upon conductivity measurements, which has a resolution similar to that of the u.v. method, is described.

Experimental

The construction of the detection cell is shown schematically in Fig. 1. To avoid disturbances of the profiles, the electrodes were constructed so that the electrolyte was surrounded by an uninterrupted cylindrical wall. For the conductivity measurements a combination of current source (0.81 kHz) and voltmeter was used (see Fig. 1). To make comparison with thermometric methods possible, a thermocouple was mounted as described by Everaerts and Verheggen[5], thermocouple and detecting electrodes being close to one another. For the present tests, the capillary tube used had an internal diameter of 0.45 mm and an external diameter of 0.7 mm. At the cathode end the capillary tube was connected to an open vessel, and at the anode end to a closed vessel.

To study the resolution of the detection system both the capillary tube and the anode compartment were filled with a solution of histidine (0.01 *M*) and histidine

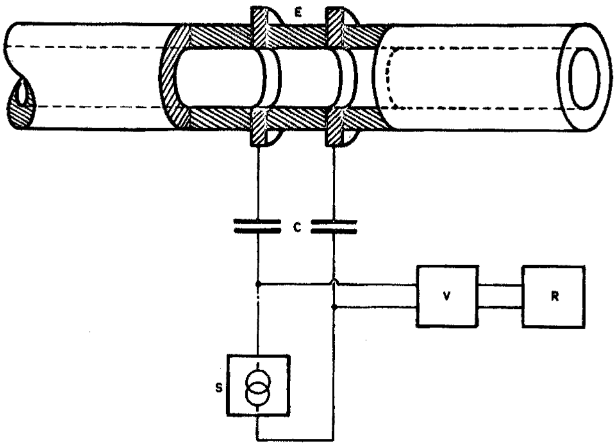

Fig. 1. Schematic representation of the detection electrode system and of the circuitry for the resistance measurement. (E) Platinum electrodes; (C) capacitors used for the separations from the d.c. voltage; (S) current source; (V) a.c. voltmeter; (R) recorder.

hydrochloride (0.01 M). The cathode compartment was filled with a solution of glumatic acid (0.01 M), as the terminating electrolyte[1]. Some electrolytic counterflow occurred caused by the production of oxygen which was visible at the anode. This counterflow influenced the measurements in two different ways: first it sharpened the boundary between the zones[6], and secondly the velocity of the boundary was reduced. To ensure isotachophoretic conditions, a high-voltage stabilized current source was applied for the driving current. The current values were chosen between 40 and 150 μA.

Results

The results of measurements, performed with different values of the driving current, are shown in Fig. 2, where the changes of the a.c. resistance between the electrodes are recorded. It can be seen that in most of these isotachopherograms the boundary passage jump is followed by a decrease in the measured resistance. This can be understood by considering that the zones have different heat productions per unit volume, hence after a boundary passage, a new thermal equilibrium has to be established. During the time interval involved, the electrical conductivity, which is temperature-dependent, will also not be constant. This explanation is supported by the fact that in Fig. 2 the slope of the decreasing parts of the isotachopherograms is proportional to the squares of the different driving currents.

For a more detailed study of the jump, experiments were made at a higher speed of the recorder paper; in Fig. 3, the measured isotachopherogram is compared with a theoretical one calculated from a rough model of the current distribution. Figure 4 shows how, in this model, the current used for the detection is distributed over the electrolyte in the neighbourhood of the detecting electrodes. Two cross-sections of the capillary tube are shown; one is perpendicular to the axis (Q), located right between the two electrodes, and the other coincides with the axis (P). When the capillary is homogeneously filled, the detection current is perpendicular to the cross-

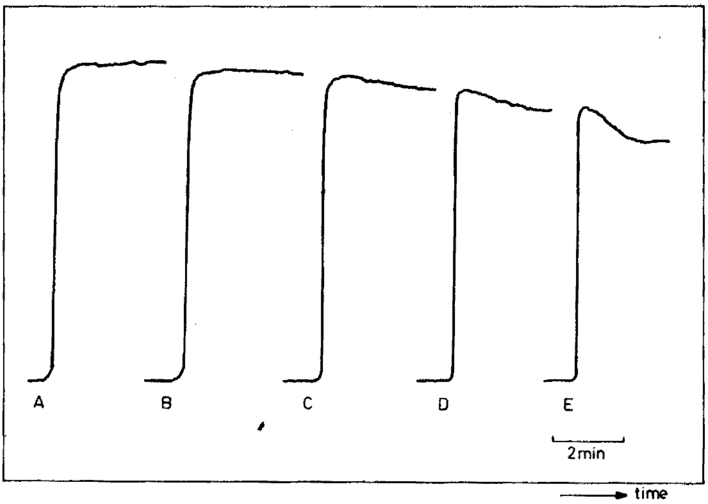

Fig. 2. Isotachopherograms measured by the a.c. resistivity method for different values of the driving current. (A) 30 μA; (B) 60 μA; (C) 80 μA; (D) 100 μA; (E) 150 μA.

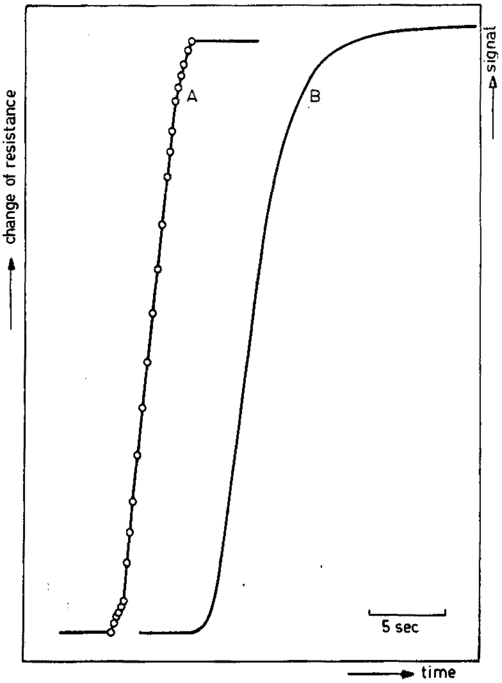

Fig. 3. Calculated (A) and measured (B) isotachopherogram for the a.c. resistivity method.

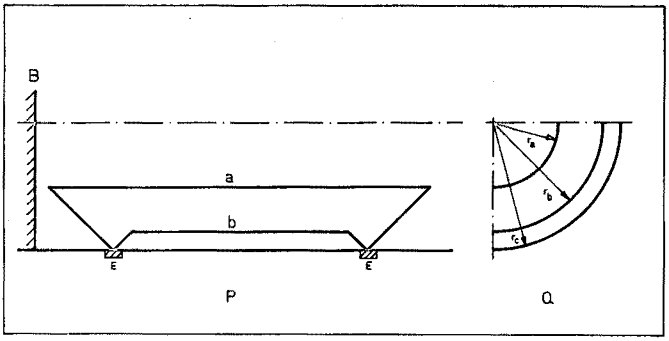

Fig. 4. Model of the current distribution in the electrolyte near the detection electrodes as used for the calculated curve in Fig. 3 (A). (E) Detection electrode; (B) zone boundary. r_a, r_b and r_c satisfy: $r_a^2 = \frac{1}{4}r_c^2$ and $r_b^2 = \frac{3}{4}r_c^2$.

section Q. The simplified current pattern is represented by parallel currents through different resistances a and b in Fig. 4 P. These two resistances are assumed to be proportional to the length of the lines a and b and to the resistivity of the electrolyte. In this model, the passing of a zone boundary can be dealt with by dividing each resistance in sections with different values of resistance per unit length. Upon a boundary passage this approximating procedure leads to a resistance *versus* time curve as shown in Fig. 3, curve A. The correspondence with the measured curve B is acceptable, apart from the deviations between the top parts of the curves. These deviations probably have three causes: (*a*) the model is highly simplified; (*b*) in the

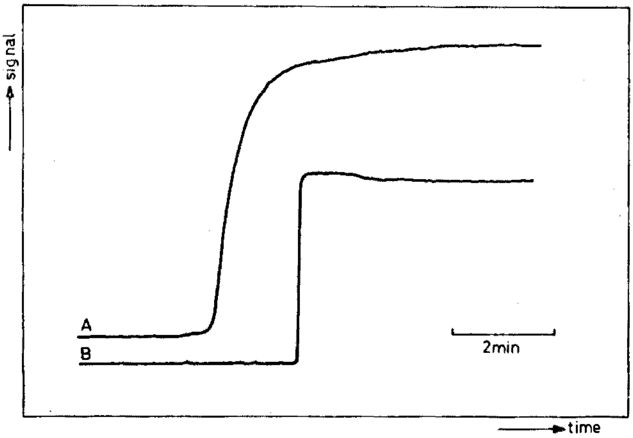

Fig. 5. Comparison of isotachopherograms. (A) Thermometric method; (B) a.c. resistivity method.

region directly behind a boundary, both the composition and the temperature of a zone may actually not be completely homogeneous; (*c*) parts of the measurement equipment introduce some time delay. Measurements with the thermometric detection method were carried out simultaneously with the resistance measurements. The two isotachopherograms are shown in Fig. 5.

Discussion

In Fig. 3 it can be seen that the boundary passage takes *ca.* 5 sec. As the zone velocity amounts to 1.5 cm min^{-1}, the measured boundary width is of the order of 1 mm. In Fig. 5A the boundary passage takes 40 sec, so here the measured boundary width is *ca.* 10 mm. It can be concluded that the resolving power of the resistivity method, being a factor of 10 better than that of the thermometric method, is similar to the resolving power of the u.v. method.

An advantage of the detection method described is that it is more universally applicable.

The research is being continued by measuring the a.c. impedance instead of the resistance, so that information about the dielectric constants can also be obtained. Additional information increase is aimed for by measuring both the real and the imaginary part of this impedance as a function of the a.c. frequency.

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A method for the spectrophotometric determination of borate in aqueous solution with curcumin

Existing methods for determining microgram amounts of borate in water, require either dehydration[1,2] or time-consuming extraction[3] or distillation[4] methods. Methods based on the reaction of water with a carboxylic anhydride[1] have to be conducted under carefully controlled conditions to ensure no loss of boron. We have found[5] that the use of the less vigorous dehydration reaction with isopropenyl acetate, with hydrochloric acid as catalyst, is convenient for the determination of borate in aqueous solution.

Equipment

The formation of complexes was conducted in polythene beakers. Glassware containing boron was cleaned with chromic acid before use. Absorption spectra were recorded on a Hilger and Watts "Ultrascan" spectrophotometer and readings made with a Unicam "SP 600" spectrophotometer.

Reagents

All reagents used, except curcumin, were of AnalaR grade.

Curcumin. Prepare a 0.125% (w/v) solution in anhydrous acetic acid.

Sulphuric–acetic acid reagent. Mix equal volumes of sulphuric and anhydrous acetic acids.

Buffer solution. Mix 90 ml of 95% ethanol, 180 g of ammonium acetate and 135 ml of anhydrous acetic acid and dilute to 1 l with distilled water.

Standard borate solutions. Prepare from disodium tetraborate decahydrate.

Procedure

(A) Transfer aliquots of the standard (5 mg B l^{-1}) borate solution, up to 1 ml, to polythene beakers, add 2 ml of anhydrous acetic acid, 3 ml of isopropenyl acetate and 0.4 ml of concentrated hydrochloric acid with swirling and leave for 30 min. Then add 4 ml of sulphuric–acetic acid reagent and 4 ml of curcumin reagent and leave the mixture for a further 60 min, before the addition of 25 ml of buffer solution to remove the protonated curcumin. Finally, measure the absorbances at 545 nm in 1-cm cells against a reagent blank.

(B) For submicrogram amounts of boron, omit the final addition of buffer and transfer the rosocyanin solution to a 250-ml separating funnel containing 150 ml of water. Then add 10 ml of acetone and 10 ml of chloroform to dissolve the complex and shake the mixture for 30 sec. Run the separated organic phase into 1-cm cells with stoppers and measure the absorbances at 545 nm against the reagent extract blank.

Results and discussion

Typical results for methods A and B are given in Table I. The linear correlations mg $B = (-0.02 \pm 0.01) + (2.100 \pm 0.004)$(Absorbance) and mg $B = (-0.001 \pm 0.005) + (1.009 \pm 0.014)$(Absorbance), respectively, showed no significant differences

TABLE I

RESULTS FOR METHODS A AND B

Method A			*Method B*		
Boron (μg)	*Absorbance*		*Boron (μg)*	*Absorbance*	
	Set 1	*Set 2*		*Set 1*	*Set 2*
1.0	0.210	0.195	0.1	0.096	0.100
2.0	0.400	0.391	0.2	0.205	0.210
3.0	0.600	0.595	0.3	0.300	0.305
4.0	0.820	0.822	0.4	0.395	0.405
5.0	1.05	1.03	0.5	0.502	0.501
Standard error of estimate	0.013	0.008	Standard error of estimate	0.002	0.001

between the sets. Benzeneboronic acid does not interfere. For the chloroform extraction, acetone was found to be the most efficient co-solvent.

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The spectrophotometric determination of iridium with N,N'-di(2-naphthyl)-*p*-phenylenediamine

In a recent article[1] a method is proposed for the spectrophotometric determination of iridium with N,N'-di(2-naphthyl)-*p*-phenylenediamine. The authors indicate that a red colouration extractable into chloroform is formed with the organic compound and iridium(IV) and an absorption spectrum is shown. No details concerning the nature of the coloured species are given although the caption to the figure alludes to the existence of an iridium complex. Work performed in this laboratory, however, does not indicate complex formation.

Figure 1 gives the absorption spectrum, scanned on a Beckman DB-G spectrophotometer, of the red coloured species obtained from the reaction of iridium-(IV) with N,N'-di(2-naphthyl)-*p*-phenylenediamine extracted into toluene. This solvent was found to give lower reagent blank values than the original chloroform used by Nasouri and Witwit[1]. The spectrum is identical with that illustrated in their article. Treatment of the organic reagent with gold(III), iron(III), or boiling with hydrogen peroxide, all produce a red species extractable into toluene. A scan of the absorption spectrum of the red colour in each case showed that the spectrum is the same as that depicted in Fig. 1, having an absorbance maximum at 485 nm.

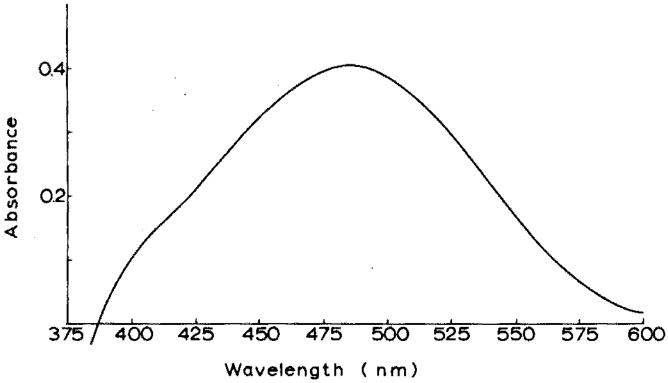
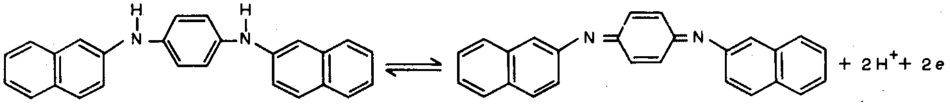


Fig. 1. Absorbance spectrum of the red species in toluene.

The aqueous and organic phases after extraction were treated with nitric and perchloric acids to destroy organic matter and investigated spectrophotometrically for iridium by production of the brown coloured hexachloroiridate(IV) anion[2]. Comparison with the absorption spectrum of a standard hexachloroiridate(IV) solution shows that no iridium is extracted into the organic phase with the red species and that all the iridium in fact remains in the aqueous phase.

All the evidence would therefore point to the red coloured species as *not* being a complex of iridium(IV) and the organic compound. The fact that gold(III), iron(III) and hydrogen peroxide all produce the same red species rather points to the occurrence of a redox reaction rather akin to the quinone–hydroquinone couple. The reaction given below can then be considered as the probable course of the production of the red species, the iridium being reduced simply to the trivalent state.



N, N′-di-(2-naphthyl)-*p*-phenylenediamine "Red species"

The principle is very akin to the determination of iridium by oxidation of leuco crystal violet[3]. In that method gold also constitutes a serious interference.

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Spectrophotometric and gravimetric determination of osmium and gold with thiosalicylamide

Thiosalicylamide has been recommended by Shome *et al.*[1,2] as a useful reagent for the determination of thallium, mercury, palladium, rhodium, ruthenium and platinum. In the present investigation, the reagent was employed for the gravimetric and spectrophotometric determination of osmium(VI or VIII) and gold(III). The brown osmium complex is precipitated quantitatively at pH 2.5–7.0 and corresponds to the formula $OsO_2(C_7H_6ONS)_2$. The gold complex, $Au(C_7H_7ONS)_3Cl$, is yellow in colour and is completely precipitated from 2.5–6.0 *N* hydrochloric acid solution. The thiosalicylamide complexes of both metals are moderately soluble in ethanol and other common organic solvents but highly soluble in ethanol–isobutyl methyl ketone mixture. The reagent solution in isobutyl methyl ketone, however, decomposes in highly acidic medium. Therefore, the osmium complex is extracted with ethanol–isobutyl methyl ketone mixture but the gold complex which is precipitated in highly acidic solutions is extracted with chloroform.

Experimental

Apparatus. A Carl-Zeiss spectrophotometer, Model PMQ II, with 1-cm quartz cells, was used for absorbance measurements. A Cambridge pH meter equipped with glass and calomel electrodes was used for pH measurements.

Standard metal solutions. An osmium solution was made by treating potassium osmate with 0.1 *M* sodium hydroxide or by dissolving osmic acid in cold distilled water. The solution was stored in the cold, and was standardized by precipitating the metal as the sulphide, followed by ignition to the metal in hydrogen.

The gold solution was prepared by dissolving pure gold(III) chloride in dilute hydrochloric acid, and was standardized by the usual oxalic acid method. Weaker working solutions of the metal ions were obtained by appropriate dilution.

Diverse ion solutions. Solutions of diverse ions were prepared by dissolving known amounts of their pure compounds in distilled water. Dilute hydrochloric acid was used where required.

Reagent solution. A 1% (w/v) solution of thiosalicylamide in 20% ethanol was used for the precipitation of osmium and gold. For spectrophotometric measurements, 0.01 *M* thiosalicylamide in ethanol was used.

All other chemicals used were of A.R. grade.

Properties of metal complexes

The osmium and gold complexes with thiosalicylamide decompose at 175° and 173° respectively. The osmium complex is stable only in weakly acidic solution whereas the gold complex is stable even in strong nonoxidizing acids. Both the complexes are readily decomposed by alkali and fairly soluble in common organic solvents. The results of analysis of pure complexes were as follows:

Osmium complex. Found: 36.20% Os, 5.15% N, 12.08% S; required for $OsO_2(C_7H_6ONS)_2$: 36.14% Os, 5.32% N, 12.16% S.

Gold complex dried at 105°. Found: 24.65% Au, 5.20% N, 12.10% S, 4.40% Cl;

required for $Au(C_7H_7ONS)_3Cl \cdot 6\,H_2O$: 24.66 % Au, 5.25 % N, 12.00 % S, 4.45 % Cl.

Gold complex dried at 135°. Found: 28.50 % Au, 5.95 % N, 13.90 % S, 5.10 % Cl; required for $Au(C_7H_7ONS)_3Cl$: 28.51 % Au, 6.07 % N, 13.88 % S and 5.15 % Cl.

Gravimetric determination of osmium and gold

Procedure. Dilute the osmium solution to about 150 ml, adjust its acidity to pH 4.0–6.0 with 10 % sodium acetate solution and precipitate the metal in the cold by adding 8–12 times the theoretical amount of thiosalicylamide solution. Allow the precipitate to stand on a hot water bath for about 1 h. Filter on a No. 4 sintered glass crucible, wash with hot water, dry at 110–120° for 2 h and weigh as $OsO_2(C_7H_6ONS)_2$.

For the determination of gold, dilute the metal solution to 150 ml and adjust its acidity to 3–4 *M* in hydrochloric acid. Warm the solution to 60–70°, add 4–5 times the theoretical amount of the reagent solution and allow the precipitate formed to stand on a hot water bath for 1 h. Filter on a No. 4 sintered glass crucible, wash with hot 10 % hydrochloric acid, dry at 135° and weigh as $Au(C_7H_7ONS)_3Cl$.

Osmium was determined in the range 7.5–30 mg and gold in the range 4.85–29.1 mg; in all cases, the error was less than 0.25 %.

Effect of acidity. The osmium complex begins to coagulate above pH 2.0, the optimum pH range for quantitative precipitation being 2.5–7.0. Gold is completely precipitated when the acidity of the solution is maintained at 2.5–6.0 *M* in hydrochloric acid; at lower acidities, the precipitate becomes slimy and does not coagulate.

Effect of diverse ions. Osmium or gold was determined with thiosalicylamide in the presence of known amounts of Co, Ni, Mn, Zn, Ti, Al, In, Cd, Cr (as their sulphates), uranyl acetate, zirconyl chloride or ammonium molybdate. Cyanide, ruthenium and rhodium interfered with the determination of osmium. Rhodium and ruthenium did not interfere with the determination of gold when the latter was precipitated from 6 *M* hydrochloric acid solution. Palladium, platinum, copper, nitric acid and other oxidizing agents, however, interfered with the determination of gold. The results are recorded in Table I.

It would be possible to separate osmium from palladium, platinum, rhodium,

TABLE I

SEPARATION OF OSMIUM AND GOLD FROM DIVERSE IONS

Gold = 9.70 mg				*Osmium = 9.50 mg*			
Foreign ion added (mg)	*Au found (mg)*	*Foreign ion added (mg)*	*Au found (mg)*	*Foreign ion added (mg)*	*Os found (mg)*	*Foreign ion added (mg)*	*Os found (mg)*
Co^{2+} (200)	9.70	Zr^{4+} (400)	9.67	Fe^{3+} (20)[a]	9.49	Mo^{6+} (80)	9.52
Ni^{2+} (200)	9.67	U^{6+} (150)	9.72	Co^{2+} (50)[a]	9.52	W^{6+} (30)	9.52
Mn^{2+} (300)	9.72	Mo^{6+} (30)	9.72	Ni^{2+} (40)[a]	9.46	U^{6+} (40)	9.49
Zn^{2+} (400)	9.72	Th^{4+} (200)	9.70	Zn^{2+} (80)[a]	9.52	Th^{4+} (80)[a]	9.52
Cd^{2+} (500)	9.70	Ir^{4+} (20)	9.70	Mn^{2+} (25)[a]	9.50	V^{5+} (40)	9.52
Ti^{4+} (40)	9.70	Ru^{3+} (13.0)	9.72	Ga^{3+} (40)[a]	9.49	Cu^{2+} (30)[b]	9.49
Al^{3+} (200)	9.72	Rh^{3+} (5.56)	9.70	In^{3+} (40)[a]	9.49	Ti^{4+} (30)[c]	9.49
In^{3+} (200)	9.72	Rh^{3+} (11.12)	9.72	Tl^{3+} (20)[a]	9.50	Ir^{4+} (10)	9.52
Ga^{3+} (100)	9.70			Al^{3+} (20)[a]	9.49		

[a] In presence of tartrate. [b] In presence of EDTA. [c] In presence of fluoride.

or ruthenium by prior reduction of Os(VI or VIII) with sulphur dioxide to Os(IV) and precipitating the foreign metal with thiosalicylamide by the earlier procedures[2]. Osmium(IV) which would remain in the filtrate, could be oxidized to osmic acid with concentrated nitric acid and distilled. The osmium content of the distillate could then be determined with thiosalicylamide as described above.

Spectrophotometric determination of osmium and gold

The osmium–thiosalicylamide complex was quantitatively extracted with isobutyl methyl ketone–ethanol mixture at pH 4.5–6.0. The brown extract showed maximal absorbance at 385 nm and obeyed Beer's law over the range 3.0–15.4 μg Os ml^{-1}. The gold complex was completely extracted in chloroform from 2.0–4.0 *M* hydrochloric acid solution. The orange-yellow extract showed an absorption peak at 460 nm and obeyed Beer's law over the range 2.78–16.68 μg Au ml^{-1}.

Procedure for osmium. Place the osmium solution in a 100-ml separating funnel and adjust its acidity to pH 4.5–6.0 with 5% sodium acetate and 1 *M* hydrochloric acid. Mix thoroughly with a known amount of the thiosalicylamide solution and place over a hot water bath for 10 min. Cool and add 0.5 g of solid potassium chloride. Add 10 ml of ethanol and extract with 5-ml portions of isobutyl methyl ketone. Collect the extracts in a 50-ml volumetric flask and dilute to the mark with isobutyl methyl ketone. Measure the absorbance of the complex at 385 nm against a reagent blank solution.

Procedure for gold. Introduce the gold solution into a 100-ml separating funnel. Adjust the acidity to 2 *M* with dilute hydrochloric acid, add a known amount of the thiosalicylamide solution and shake well. Allow the mixture to stand for 10–15 min. Extract the yellow precipitate with four 5-ml portions of chloroform. Dilute the combined extracts to 25 ml with chloroform and measure the absorbance at 460 nm against a reagent blank solution.

The absorbance curves of the solutions of the above metal complexes are shown in Fig. 1.

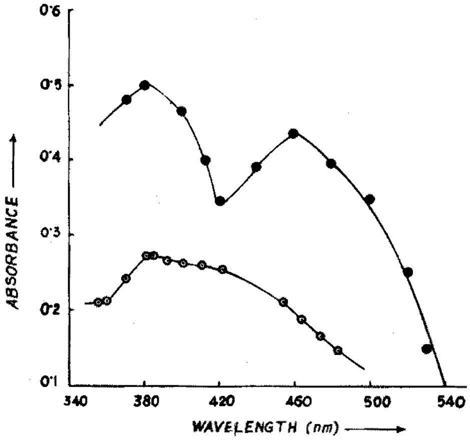

Fig. 1. Absorbance curves of metal–thiosalicylamide complexes. (○) Osmium–thiosalicylamide complex in isobutyl methyl ketone–ethanol mixture. [Os] = 7.70 μg ml^{-1}. (●) Gold–thiosalicylamide complex in chloroform. [Au] = 8.52 μg ml^{-1}.

Effect of pH. The pH of the osmium solution was adjusted with 5% sodium acetate solution and dilute hydrochloric acid. The pH values of the aqueous layers were measured after the extraction of the osmium–thiosalicylamide complex. It was observed that 100% extraction of the osmium complex could be made at pH 4.5–6.0. Below pH 3.50, the reagent was partly oxidized and anomalous results were obtained.

Gold–thiosalicylamide complex was quantitatively extracted with chloroform from 2.0–4.0 *M* hydrochloric acid solution.

Effect of diverse ions. Osmium and gold could separately be determined in presence of appreciable amounts of diverse ions by following the above procedures. The tolerance limits (*i.e.* concentrations causing an error less than ±2%) are recorded in Table II, EDTA, tartrate, fluoride and phosphate could be tolerated in amounts up to 20 mg but cyanide interfered, as did platinum, rhodium and ruthenium.

TABLE II

EFFECT OF DIVERSE IONS IN THE SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM AND GOLD

Osmium (187.1 μg)				*Gold* (208.8 μg)			
Diverse ion	*Amount tolerated (μg)*	*Diverse ion*	*Amount tolerated (μg)*	*Diverse ion*	*Amount tolerated (μg)*	*Diverse ion*	*Amount tolerated (μg)*
Mn^{2+}	1000[a]	Th^{4+}	1000[a]	Mn^{2+}	5000	Ti^{4+}	1000
Ni^{2+}	1500[a]	V^{5+}	500	Co^{2+}	5000	Rh^{3+}	500
Co^{2+}	2000[a]	Mo^{6+}	2000	Ni^{2+}	4000	Th^{4+}	5000
Zn^{2+}	3000[a]	W^{6+}	1500	Zn^{2+}	3000	V^{5+}	150[d]
Fe^{3+}	1500[a]	Ti^{4+}	600[b]	Cd^{2+}	5000	U^{6+}	6000
Cr^{3+}	1000[a]	Cu^{2+}	500[c]	Al^{3+}	5000		
Al^{3+}	1200[a]	Pd^{2+}	100	Ga^{3+}	1000		
Ga^{3+}	1500[a]	Au^{3+}	100	In^{3+}	1000		
In^{3+}	1000[a]	Ir^{4+}	100	Cr^{3+}	5000		
Tl^{3+}	800[a]			Fe^{3+}	500[d]		

[a] In presence of fluoride. [b] In presence of tartrate. [c] In presence of EDTA. [d] In presence of phosphate.

Effect of reagent concentration and nature of the complex. It was found that osmium(VI) was completely extracted when the reagent concentration was eight times the molar concentration of the metal ion. For osmium(VIII), the reagent concentration required for complete extraction was 10 times that of the metal ion. The results of the mole-ratio method[3] for the study of the nature of osmium complex were inconclusive.

The empirical formula of the gold(III)–thiosalicylamide complex was determined by the mole-ratio method[3], which indicated the formation of a 1:4 complex; this was supported by the slope-ratio method[4]. The dissociation constant of this complex in chloroform was determined from the mole-ratio curve[4] to be $1.576 \cdot 10^{-22}$.

Molar absorptivity, sensitivity, precision and accuracy. These data for the metal complexes are given in Table III.

Discussion

Analytical reagents for the precipitation of osmium and gold in direct weighing

TABLE III

MOLAR ABSORPTIVITY, SENSITIVITY, PRECISION AND ACCURACY

Complex	*Molar absorptivity*	*Sensitivity ($\mu g\ cm^{-2}$)*	*Relative standard deviation (%)*	*Relative mean error (%)*
Osmium–thiosalicylamide	$66.14 \cdot 10^2$	0.0287	0.63	0.24
Gold–thiosalicylamide	$10.06 \cdot 10^3$	0.0196	0.61	0.25

forms are few in number. Thiosalicylamide is an excellent gravimetric reagent for both the metals, since it is highly soluble in hot water and easily forms water-insoluble complexes of definite composition which can be freed from excess reagent by washing. Both gold and osmium can be separated from almost all the base metals with thiosalicylamide as precipitant. The metal complexes are easily extractable in organic solvents and are well suited for the spectrophotometric determination of trace amounts of the metals.

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2-Amino-4-methylthiazole as a reagent for the gravimetric determination and extraction of mercury(II)*

As a part of studies on reagents analogous to 2-mercaptobenzothiazole, 2-aminobenzothiazole was recently reported as a selective reagent for the gravimetric determination[1] and extraction[2] of mercury(II). With the possibility of developing better reagents, these studies were extended to 2-aminothiazole, 2-amino-4-phenylthiazole, and 2-amino-4-methylthiazole. On the basis of the comparative solubility of these reagents and their mercury(II) complexes, and of their selectivity, detailed investigations were carried out only on 2-amino-4-methylthiazole. Like 2-aminobenzothiazoles[3,4], all 2-aminothiazoles exhibit an enamine–ketimide tautomerism[5]. The ketimide form offers a good possibility of complexation with different cations. 2-Amino-4-methylthiazole was found to give precipitates with silver(I), mercury(II), and gold(III) only. Since there is a dearth of good gravimetric reagents for mercury(II), the present reagent was developed for this cation. Higher aqueous solubility and selectivity make this reagent even better than 2-aminobenzothiazole. Unlike 2-aminobenzothiazole, neither the silver(I) complex nor the gold(III) complex extracts with mercury(II) complex, which could provide a useful separation in activation analysis.

Reagents and apparatus

All the reagents were of analytical grade. Thiazoles (Aldrich Chemical Co., U.S.A.) were recrystallized from alcohol, and their melting points were checked.

Walpole, Thiel, Schulz, and Coch buffers[6] prepared in twice-distilled water were used. Buffers involving chloride ions were avoided because of the extraction of mercury(II)–chloro complexes in the solvents investigated[7].

^{110m}Ag (as $AgNO_3$), ^{198}Au (as $HAuCl_4$), and ^{203}Hg (as $Hg(NO_3)_2$) isotopes (Bhabha Atomic Research Centre, Bombay) were used as tracers in radiometric titrations and to study the distribution ratios in the extractions. The γ-activity was measured on a flat 25 x 25 mm NaI(Tl) crystal coupled to a single-channel analyzer. An additional assembly was mounted on the crystal head to hold the beakers in reproducible geometry. Thermogravimetric studies were done on a Stanton thermobalance.

Mercury(II) chloride solution was standardized by the Reinecke salt method[8]. The ligand solution was standardized by determining its sulphur content. In liquid–liquid extraction studies, equilibrated solvents were used.

Reactions with metal ions

Qualitative tests with a number of metal ions (36) were performed with each of the three reagents (Table I).

The mercury(II) complexes were found to be slightly soluble in alcohol at all concentrations. 2-Amino-4-methylthiazole was selected for further studies as it is fairly soluble in water.

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* Presented at the Convention of Chemists (India), IIT Madras, December 3, 1970.

TABLE I

QUALITATIVE REACTION BEHAVIOUR OF THE REAGENTS

Reagent	*Metal ions giving positive test*
2-Aminothiazole (solution in 95% alcohol)	Ag(I), light yellow; Hg(II), yellow; Pd(II), orange; Cu(II), light brown changing to dark brown; Cd(II), white; Sn(II) and Sn(IV), white; and Au(III), light yellow.
2-Amino-4-phenylthiazole (aqueous solution)	Ag(I), white changing to yellow; Hg(II), white; and Au(III), yellow.
2-Amino-4-methylthiazole (aqueous solution)	Ag(I), light yellow; Hg(II), light yellow; and Au(III), dark brown.

pH range for maximum precipitation and composition of the complex

Radiometric titrations were done to establish the pH of maximum precipitation and the composition of the complex. The procedure was the same as described earlier[1]; the mercury(II) solutions were buffered because of the hydrogen ion released during complexation. Within experimental error, the ligand completely precipitates mercury(II) above pH 8.4. At pH 9.20 the ligand–metal ratio in the complex was found to be 1:1.

Drying temperature and stability of the complex

Thermal analysis of an air-dried sample of the complex was done on a Stanton thermobalance at a heating rate of 5.3° min^{-1}. The complex remained stable up to 170° after which it gradually lost weight; 90–100° was chosen as the drying temperature.

Analytical procedure

To samples containing 20–150 mg of mercury(II), an aqueous $2.5 \cdot 10^{-2}$ *M* solution of the reagent was added in slight stoicheiometric excess. This was followed by the addition of buffer pH 9.20. The precipitate was filtered off through a sintered glass crucible (porosity 4) and washed with water. The precipitate was dried at 90–100° for 1 h and weighed as Hg $C_4H_4N_2S$. The error was within ± 1%.

There was no evidence of bias in the determination of 100 mg of mercury(II) and the relative standard deviation was 0.67% (16 results).

Effect of diverse ions

Silver(I) and gold(III) interfered. No interference was caused by fluoride, oxalate, citrate, and tartrate, but iodide, cyanide, sulphide, thiosulphate and EDTA interfered.

Determination of 2-amino-4-methylthiazole

The reagent could be determined gravimetrically by a procedure similar to that used for mercury(II). When a slight excess of mercury(II) was added and the solution buffered to pH 9.20, the results, on average, were 1–2% low.

Extraction behaviour of mercury(II) complex

The procedure was the same as outlined earlier[2]. Experiments were run in duplicate at room temperature (28 ± 2°); blanks with different buffers were also run to avoid any confusion with the extraction of mercury(II)–buffer species[9]. The reproducibility was checked by performing replicate extractions into amyl acetate at pH 8.35 to give a mean distribution ratio of 8.02. The distribution ratios showed a

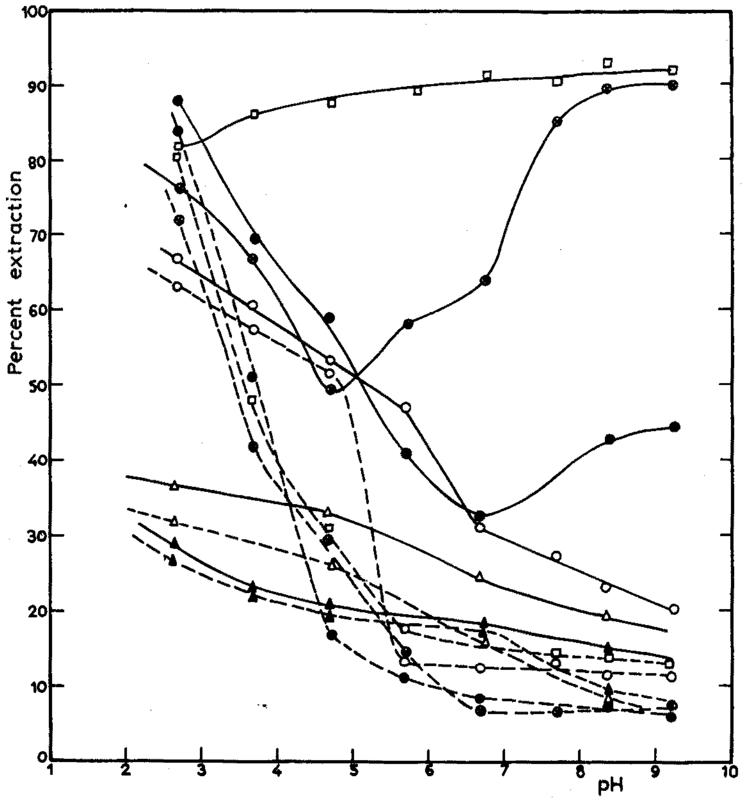

Fig. 1. Effect of pH on the extraction of Hg(II)–2-amino-4-methylthiazole complex in different solvents. (▲) Chloroform, (△) carbon tetrachloride, (●) ethyl acetate, (○) di-isopropylether, (⊗) amyl acetate, (□) ethyl acetate–di-isopropylether (1:1). (---) Blanks.

TABLE II

EXTRACTION BEHAVIOUR OF MERCURY(II) COMPLEX IN SOLVENT MIXTURE AT pH 7.7

Composition of the system (v/v) *Ethyl acetate: di-isopropylether*	*% Extraction*	*Blank*
30:70	58.40	15.90
40:60	70.60	16.10
50:50	89.50	16.12
60:40	88.70	15.90
70:30	90.00	16.00

standard deviation of *ca.* 0.2%.

The effects of pH on the percentage extraction of the mercury(II) complex in different solvents are given in Fig. 1; the broken lines show the blanks obtained with the buffers. The complex showed negligible extraction in chloroform and carbon tetrachloride. Ethyl acetate and di-isopropylether were more satisfactory solvents, and a mixture of the two was finally used[2]. The results obtained for the extraction of the complex with solvent mixtures of differing compositions are given in Table II.

Effect of diverse anions. The effect of anions which might suppress the extraction was studied: Oxalate, citrate, tartrate, chloride, bromide and fluoride did not affect the distribution ratios significantly. EDTA, iodide, cyanide and thiocyanate interfered.

Extraction behaviour of silver(I) and gold(III) complexes

The extraction of the silver(I) complex is shown in Fig. 2. Maximal extraction occurs up to pH 4.5; blanks in all solvents were similar (7–11%). The complex had a mean distribution ratio of 8.90 at pH 3.7 with amyl acetate as a solvent. Cl^-, Br^-, I^-, F^-, SCN^-, CN^-, citrate, tartrate, oxalate and EDTA interfered. The gold(III) complex showed poor (≤ 9%) extraction throughout the pH range in the solvents investigated.

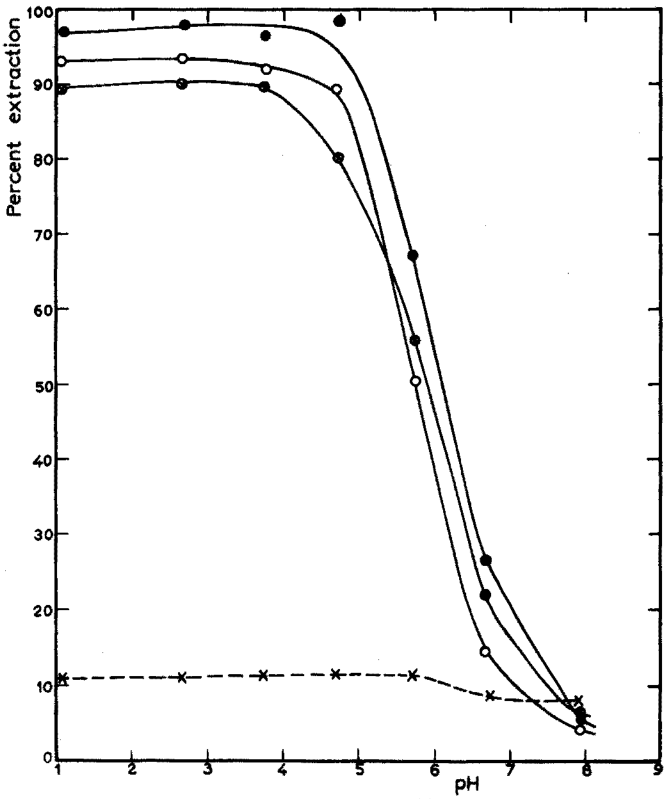

Fig. 2. Effect of pH on the extraction of Ag(I)–2-amino-4-methylthiazole complex in different solvents. (○) Di-isopropylether, (●) ethyl acetate, (⊗) amyl acetate. (× --- ×) Average blanks.

Separation of mercury(II) from silver(I) and gold(III)

Above pH 8.4, the mercury(II) complex can be extracted quantitatively into amyl acetate, whereas the silver(I) complex shows negligible extraction. Chloride, bromide, oxalate, citrate, or tartrate do not affect the extraction of mercury(II) whereas they prevent the extraction of silver(I). Mercury(II) can be separated from silver(I) by either of these ways. As the gold(III) complex shows very poor extraction, mercury(II) can be easily separated from it.

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Separation of iodides, tellurites and tellurates by extraction with ethyl acetate–methyl isobutyl ketone mixtures

Several methods are known for the separation of tellurium from iodine. Distillation has been frequently used[1-3]. Ion exchange is possible with tellurium(IV) and iodide being adsorbed on an anion-exchange resin, while tellurium(VI) passes through; iodide is then eluted by weakly acid solution, and tellurium(IV) at higher acidity[4]. Extraction methods have been applied with carbon tetrachloride[5], or with tributylphosphate (TBP)[6]. In the latter method, iodine is extracted with TBP from 0.2 *M* hydrochloric acid in the presence of hydrogen peroxide, and tellurium(IV) and (VI) remain in the aqueous phase; when the hydrochloric acid concentration is increased to 4 *M*, tellurium(IV) can be extracted with TBP while tellurium(VI) remains in the aqueous phase.

Tellurium(IV) is extracted to the extent of only 34% by ether from 6 *M* hydrochloric acid solution[7], but is more readily extracted by ketones from hydrochloric acid solutions[8]. Alcohols and higher ethers also extract tellurium, while lower ethers are poor extractants[8]. When extraction with ketones is applied, an increase in the distribution coefficient of tellurium(IV) is observed when its concentration in the aqueous phase is decreased, owing to increased dissociation of the extracted compound in solvents of higher dielectric constants.

The present paper describes the use of a mixture of ethyl acetate and methyl isobutyl ketone for separation of tellurium and iodine. Iodine is extracted from 0.1 *M* hydrochloric acid solution in the presence of hydrogen peroxide; tellurium(IV) is extracted from 5 *M* hydrochloric acid and tellurium(VI) remains in the aqueous phase.

An enhancement of the solvent extraction is observed when this mixture of organic extractants is used. There appears to be a synergic effect; one of the extractants neutralizes the charge on the metallic ion, thus forming a neutral complex or chelate, while the other solvent replaces the coordinated water in the complex thus making it insoluble in the aqueous phase. Another possible explanation is based on the formation of a coordinatively unsaturated neutral complex which can add one or more molecules which are electron donors. Such complex organic adducts show very often a better solubility in organic than in aqueous phases.

Experimental

Extraction procedure. Prepare 10 ml of a 0.1 *M* hydrochloric acid solution containing 0.2 mg ml^{-1} each of iodide, tellurium(IV) and tellurium(VI). Add 1 ml of 3% hydrogen peroxide solution and 10 ml of a mixture containing ethyl acetate and methyl isobutyl ketone at a ratio of 2:1. Saturatethe organic phase with hydrochloric acid of the same concentration as that of the test solution. Separate iodine by three extractions with 10-ml portions of the extractant mixture. After the separation of the iodine, add hydrochloric acid to the aqueous phase to adjust the acidity to 5 *M*. Extract tellurium(IV) with 10-ml, 5-ml and 5-ml portions of the solvent mixture. Tellurium(VI) remains in the aqueous phase.

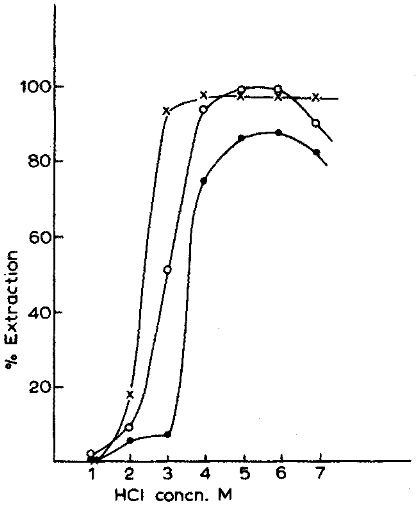
Measurement of the distribution coefficients. The distribution coefficients were determined by using active tellurium dioxide containing a mixture of the isotopes ^{125m}Te, ^{127}Te, ^{127m}Te, ^{129}Te and ^{129m}Te, the specific activity of tellurium being of the order of mCi. This mixture was obtained by irradiation of a sample during 10 days at a neutron flux of $3.7 \cdot 10^{13}$ n cm^{-2} sec^{-1}. It should be mentioned that the tellurium dioxide was used only 6 months after the irradiation, so that the ^{131}I isotope had completely decayed. ^{131}I was formed by the reaction ^{130}Te(n, γ) ^{130}Te $\xrightarrow{\beta}$ ^{131}I.

By measuring the activity of the organic and aqueous phases, the distribution coefficients were determined in the aqueous phase at different hydrochloric acid concentrations and for different solvent mixtures. The activity was measured with a well-type NaI(Tl) Nuclear Chicago DS5-5 scintillation counter, a counting time of 1 min being used. A correction was applied for the background activity, and the geometry of the system was kept constant.

Results and discussion

Figure 1 shows the percentage extraction of tellurium(IV) at various acidities of the aqueous phase with different solvents. It is clear that better extraction efficiency is obtained when the solvent mixture is used.

The tracer technique was also used to study the behaviour of tellurium(VI). Active tellurium dioxide oxidized by 8% ammonium persulphate in acidic solution was used as tracer; the completeness of the oxidation was checked by spectrophotometric determination of tellurium(IV) with sodium diethyldithiocarbamate at pH 2



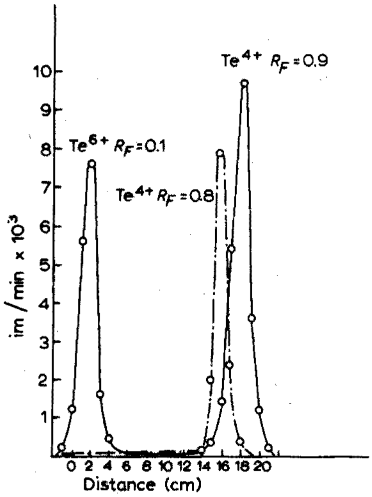


Fig. 1. Dependence of the percentage extraction of tellurium(IV) on the acidity of the aqueous phase for different solvents. (●) Ethyl acetate; (×) methyl isobutyl ketone; (○) ethyl acetate + methyl isobutyl ketone.

Fig. 2. Chromatograms of tellurite and tellurate. (————) Without prior extraction; (-·-·-) after extraction.

with measurement at 460 nm[9]. When the oxidized tellurium samples were extracted with the ethyl acetate–methyl isobutyl ketone mixture at different hydrochloric acid concentrations, no transfer of tellurium(VI) to the organic phase was found.

The effectiveness of the separation of tellurium(IV) from tellurium(VI) is shown in Table I.

TABLE I

SEPARATION OF TELLURIUM(IV) FROM TELLURIUM(VI)

Sample no.	*Activity taken (counts min^{-1})*		*Activity after separation (counts min^{-1})*				
	Te(IV)	*Te(VI)*	*I$^-$ fraction*	*Te(IV) fraction*	*Te(VI) fraction*	*Deviation (%)*	
						Te(IV)	*Te(VI)*
1	50762	55618	4	49514	53720	−2.4	−3.4
2	56320	56100	5	54900	54268	−2.4	−3.2

An additional chromatographic control[10] was performed to determine the extent of the oxidation of tellurium(IV). Tellurium(IV) was separated from Te(VI) in 90% acetone–5% HCl–5% H_2O solvent; 5–10-μl samples from the organic and aqueous phases were applied on separate bands of Whatman No. 1 paper (2.5 × 22 cm), which were developed for 5 h at room temperature. The distribution was measured at every cm of the band after drying at room temperature. Tellurium(VI) remained at the start, while tellurium(IV) moved with the mobile phase. Figure 2 shows the chromatograms obtained for a mixture of tellurite and tellurate in 5 *M* hydrochloric acid without prior extraction, and for tellurite after extraction. It can be seen that extraction causes a decrease in the R_F value of tellurium(IV) from 0.9 to 0.8, whereas the R_F value for tellurium(VI) remains constant at 0.1. The chromatograms proved that no mixing of the valence states occurred.

Separation of iodides

^{131}I isotope was used as tracer in studying the extraction of iodide. The extraction was performed in the presence of inactive carrier potassium iodide and hydrogen peroxide. The results are given in Table II.

TABLE II

EXTRACTION OF IODIDE FROM TELLURIUM(IV) AND TELLURIUM(VI)

HCl concn. in aqueous phase (M)	*Activity (counts min^{-1})*[a]	
	Organic phase Iodine	*Aqueous phase Te(IV) Te(VI)*
0.1	13,870	27
0.2	13,900	45

[a] Activity of iodine = 14,080 counts min^{-1}.

Application

This procedure was used to determine tellurium(IV) in a sample of telluric acid irradiated at this Institute. The analysis showed the presence of 2.35% of tellurium(IV) in the sample. An inspection of both organic and aqueous phases by γ-spectrometry showed that there was no iodine in tellurium.

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Solvent extraction of uranium(VI) with trioctylphosphine oxide in the presence of aromatic carboxylic acids

It has already been shown[1,2] that benzoic acid has a synergic effect on the solvent extraction of thorium and uranium(VI) from slightly acidic medium using a carbon tetrachloride solution of trioctylphosphine oxide (TOPO). This extraction is quite selective and effective and it was applied to the separation of thorium and uranium from accompanying elements in rock analysis[3]. The purpose of the investigation described here was to study comparatively the effect of other aromatic carboxylic acids on the solvent extraction of uranium with TOPO in carbon tetrachloride. A synergic effect was expected depending on the composition and strength of the acid. Benzoic acid, its *ortho*-derivatives, and benzene derivatives with an acidic side-chain were examined (see Table I). Of the acids listed in Table I, only the effect of salicylic acid has previously been studied on the extraction of uranium(VI) with hexone[4].

TABLE I

SOLVENT EXTRACTION OF URANIUM (1000 μg) WITH A MIXTURE OF 0.02 M TOPO AND 0.01 M ACID

Acid	*Formula*	*pK*	*D*	
			3.85 *pH*	4.90 *pH*
Phenylpropiolic acid	$C_6H_5C{\equiv}CCOOH$	2.23	214.0	363.0
o-Chlorobenzoic acid	$C_6H_4(Cl)COOH$	2.92	105.0	223.0
Salicylic acid	$C_6H_4(OH)COOH$	2.97	365.0	693.0
Benzoic acid	C_6H_5COOH	4.17	21.8	93.9
trans-Cinnamic acid	$C_6H_5CH{=}CHCOOH$	4.44	14.9	32.9
Hydroxycinnamic acid	$C_6H_5CH_2CH_2COOH$	4.74	6.9	37.4
o-Nitrobenzoic acid[a]	$C_6H_4(NO_3)COOH$	2.21	4.0	8.4

[a] Owing to restricted solubility the concentration of *o*-nitrobenzoic acid was 0.0015 M.

Experimental

The experiments were done with a solution of uranyl nitrate in 0.01 M nitric acid. The uranium concentration was determined gravimetrically with 8-hydroxyquinoline[5].

Solutions of pure recrystallized organic acids in carbon tetrachloride were prepared, the concentrations being $5\cdot10^{-3}$, $1\cdot10^{-2}$ and $2\cdot10^{-2}$ M. Because of the limited solubility of *o*-nitrobenzoic acid in carbon tetrachloride the solution was only $3\cdot10^{-3}$ M. A $4\cdot10^{-2}$ M solution of TOPO in carbon tetrachloride was used; the free acids were removed from this solution by stripping three times with a 4 % sodium hydroxide solution and then washing with water.

Extractions were carried out in Jena glass 50-ml vessels provided with ground-glass stoppers. For each test, 1000 μg of uranium in 10 ml of aqueous solution at the appropriate pH value was extracted with 10 ml of organic solution obtained by mixing 5 ml of $4\cdot10^{-2}$ M TOPO and 5 ml of a solution of the organic acid; the mixtures were shaken at 200 r.p.m. until equilibrium was attained (10 min). The two phases were separated by centrifugation. The distribution coefficient was found by determining uranium in an aliquot part of the aqueous phase photometrically by means of arsenazo III in monochloroacetate-buffered solutions[6]. Periodically the uranium concentration was checked in the organic phase by re-extraction with the arsenazo III solution[7].

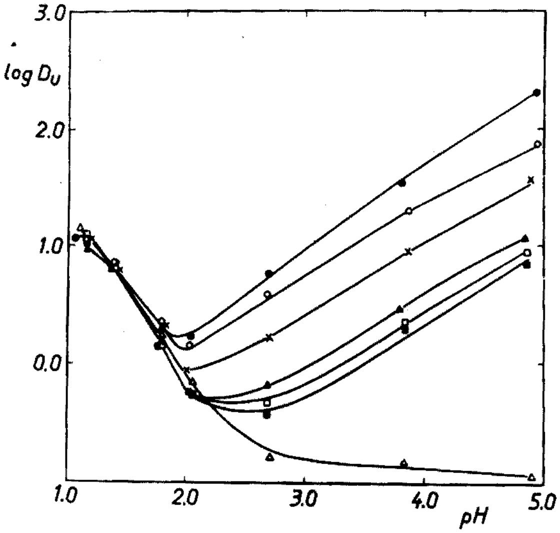

Fig. 1. Dependence of log D_U on pH of the aqueous phase in the extraction of uranium with carbon tetrachloride solutions of $2\cdot10^{-2}$ *M* TOPO (△) and a mixture of $2\cdot10^{-2}$ *M* TOPO and $2.5\cdot10^{-3}$ *M* acid. (○) $C_6H_5C{\equiv}CCOOH$; (×) $C_6H_4(Cl)COOH$; (●) $C_6H_4(OH)COOH$; (▲) C_6H_5COOH; (□) $C_6H_5CH{=}CHCOOH$; (■) $C_6H_5CH_2CH_2COOH$.

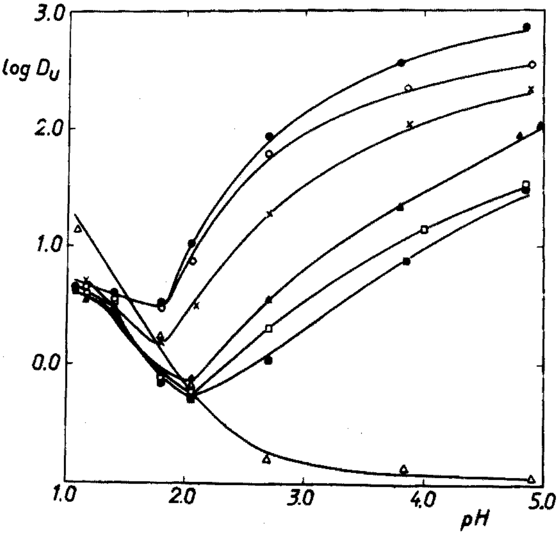

Fig. 2. Dependence of log D_U on pH of the aqueous phase in the extraction of uranium with carbon tetrachloride solutions of $2\cdot10^{-2}$ *M* TOPO (△) and a mixture of $2\cdot10^{-2}$ *M* TOPO and $1\cdot10^{-2}$ *M* acid. Designation of acids as in Fig. 1.

Results and discussion

Figures 1 and 2 show the extraction curves of uranium with 0.02 *M* solutions of TOPO in the presence of $2.5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ *M* concentrations of different aromatic carboxylic acids. To facilitate comparison the extraction curve of uranium in the absence of organic acids is also given. The curves involve two regions: a region of antagonistic action (pH 1–1.80) and a region of synergic action (pH > 1.80). At pH 1.1 the antagonistic action of the acid is best displayed at the highest concentration used—$1.0 \cdot 10^{-2}$ *M* (see Fig. 2). Curves of a similar nature were obtained when the concentration of organic acid was $5 \cdot 10^{-3}$ *M*; for these concentrations, the curves lay intermediately between those shown in Figs. 1 and 2. The dependence of log *D* on the p*K* value of the acids for pH 1.1 of the aqueous phase is linear (Fig. 3). It can be seen from Figs. 1 and 2 that the antagonistic effect of the organic acids changes to a synergic effect at different pH values depending on the acid strength. The synergic effect, *S*, is defined as the ratio of the distribution coefficients of uranium on the extraction with a mixture of TOPO and organic acid, to those on extraction with only TOPO:

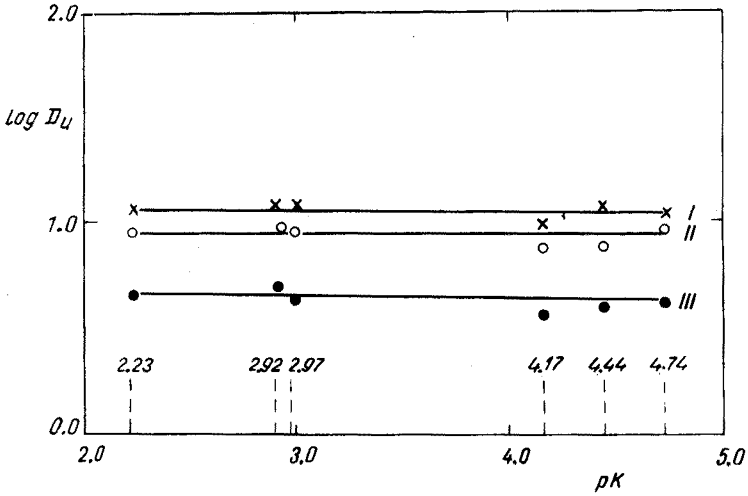

Fig. 3. Dependence of log D_U on p*K* of the acids at pH 1.10 for various concentrations of the acids. (×) $2.5 \cdot 10^{-3}$ *M*; (○) $5 \cdot 10^{-3}$ *M*; (●) $1.0 \cdot 10^{-2}$ *M*. For acids corresponding to p*K* values, see Table I.

$$S = D_{\text{TOPO+acid}}/D_{\text{TOPO}}.$$

The dependence of log *S* on the p*K* value of the organic acid for pH 3.85 in the aqueous phase is shown in Fig. 4. The points corresponding to a given acid concentration fall on straight lines with the exception of salicylic acid; the deviation may be due to a different type of bonding of this acid to uranium.

The various effects observed in the solvent extraction of uranium(VI) with TOPO in the presence of aromatic carboxylic acids may be explained as follows. At low pH values the acids are protonated and are therefore present predominantly in the organic phase; here, the acids form adducts with TOPO, thus decreasing its active concentration. When the pH is increased, the acids are dissociated, the extent

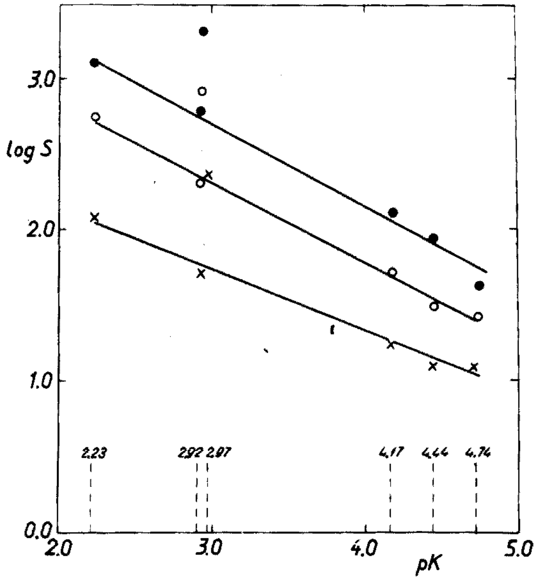

Fig. 4. Dependence of log S on pK of the acids at pH 3.85 for three different concentrations of the acids. (×) $2.5\cdot10^{-3}$ M; (○) $5\cdot10^{-3}$ M; (●) $1.0\cdot10^{-2}$ M.

of dissociation depending on their pK values, and are thus transferred to the aqueous phase, where they form complexes with uranium(VI) which are further solvated with TOPO and extracted. The stronger the organic acid, the greater its synergic effect at a given pH value. The distribution coefficients for uranium at two pH values (3.80 and 4.80) are given in Table I.

Analytical applications

The high distribution coefficient of uranium(VI) on extraction with a mixture of carbon tetrachloride solutions of TOPO and salicylic acid at pH 5 may be used for the separation of uranium from various interfering elements, *e.g.* rare earth elements,

TABLE II

EXTRACTION OF URANIUM FROM INTERFERING ELEMENTS WITH TOPO AND SALICYLIC ACID

Element (*Me*)	*Ratio U/Me*	*U* (*μg*)	
		Taken	*Found*
Lanthanum	1:100	47.0	47.0
Yttrium	1:100	47.0	46.0
Gadolinium	1:100	47.0	46.6
Cerium	1:100	47.0	46.8
Thorium	1:100	47.0	46.8
Zirconium	1:100	47.0	46.6
Iron	1:100	47.0	46.0
Iron	1:1000	47.0	46.3
Iron	1:2600	18.8	19.6

thorium, zirconium and iron, with the possibility of subsequent photometric determination with arsenazo III. Interfering elements can be masked with a 0.02 *M* solution of EDTA; at pH 5, EDTA did not interfere with the solvent extraction of uranium. The ratios of uranium to interfering element which were investigated are shown in Table II. The extraction (one-fold) was done with 0.02 *M* TOPO and 0.005 *M* salicylic acid at pH 5. The uranium re-extraction was done with arsenazo III solutions.

Conclusion

In the extraction of uranium(VI) in the pH region 1–5 with TOPO in the presence of aromatic monocarboxylic acids, the action of the organic acids varies from antagonistic below pH 1.8 to synergic above pH 2.0. The antagonistic effect depends entirely on the acid concentration. The degree of the synergic effect depends linearly on the p*K* values of the organic acids, except in the case of salicylic acid for which an unusually high synergic effect is observed.

An extractive separation of uranium(VI) is possible with a mixture of TOPO and salicylic acid at *ca.* pH 5, from various elements which interfere with its photometric determination by means of arsenazo III. These elements are rare earths, thorium, zirconium and iron.

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A rapid procedure for the separation of technetium from a molybdenum matrix and ruthenium

In a search[1] for the short-lived ruthenium-92 isotope produced by cyclotron bombardment of an enriched molybdenum-92 target, a very rapid decontamination of ruthenium from technetium was necessary, because short-lived isotopes of technetium would seriously mask the ruthenium activity. Especially ^{92}Tc, which has a much higher formation cross-section for the 36-MeV ^{3}He particles on ^{92}Mo than ^{92}Ru, would seriously affect the sensitivity for ^{92}Ru; ^{92}Tc has a 4.3-min half-life, which is short enough for high activities to be produced in brief bombardments but long enough for cooling periods to be impossible without loss of ^{92}Ru-activity. A separation of ruthenium from molybdenum was not considered necessary as the molybdenum yields very little molybdenum activity on ^{3}He-bombardment. The expected half-life of the ^{92}Ru made it desirable for the separation to be finished within *ca.* 1 min, removal of the sample from the irradiation site included. Accordingly, it was necessary to have a one-step separation, as well as complete dissolution of the molybdenum metal sample within a few seconds, and a rapid means of obtaining a suitable medium for the separation. Precipitation of technetium with large cations such as Ag^+, Cs^+, Tl^+ and $(C_6H_5)_4As^+$ has been used for isolation of technetium, and Flegenheimer and Seelmann-Eggebert[2] could coprecipitate technetium with tetraphenylarsoniumperrhenate and filter the sample in 5–6 sec. However, ruthenium also precipitates with the tetraphenylarsonium ion[3], so that this separation cannot be used for the present separation. A coprecipitation of Ru(III) and RuNO(II) on iron hydroxide[4] proved to be too time-consuming, as are distillation procedures[5] or extraction of ruthenium with oxine into chloroform[6].

Extraction procedures seemed to offer the quickest separations. However, many procedures described start from a medium in which molybdenum metal is insoluble or very slowly soluble, *i.e.* HNO_3[7,8], H_2SO_4[9,10], H_3PO_4[11], H_3PO_3[12] or HF[13]. Extraction with pyridine[14,15] or with quaternary amines[16] from aqueous sodium hydroxide, which can easily be converted to an acid solution, were most promising, although disagreement exists over the quantitative character of the pyridine extractions. Gerlit[17] claimed that the distribution constant of Tc(VII) between pyridine and 5 *M* sodium hydroxide was only 39 and that Mo(VI) and Ru(IV) were substantially extracted, whereas Goishi and Libby[14] found a distribution constant equal to 778 for Tc(VII). Extraction from aqueous sodium hydroxide solutions with both pyridine and quaternary amines were tested by us, with ^{99}Mo, ^{94}Tc and ^{97}Ru as tracers.

Experimental

Tracers used. ^{99}Mo was produced by neutron irradiation of molybdenum metal in the Safari reactor of the Atomic Energy Board (Pelindaba, South Africa). ^{94}Tc and ^{97}Ru were produced simultaneously by α-bombardment of a molybdenum metal target in the C.S.I.R. cyclotron.

Dissolution of the target. Molybdenum metal can be dissolved in hot concentrated nitric or sulphuric acid, but the dissolution is time-consuming. Mixtures of nitric and hydrochloric acids in varying proportions were therefore tested; a (3:1) mixture of HNO_3: HCl was found to be most efficient, a thin foil of molybdenum metal (3 mg cm^{-2}) being dissolved in 2–3 sec.

Conversion to a suitable separation medium. According to Maeck *et al.*[16] the 8 and 7 valence states of Group VIIIA are almost quantitatively extracted by quaternary amines from 0–5 *M* sodium hydroxide, while Ru(III)—the most stable valency of ruthenium—is not extracted. An extraction of technetium(VII) is also possible with pyridine[14,15] from the hydroxide medium. As the aqueous hydroxide medium can be easily obtained by making the acidic solvent alkaline, both extraction procedures were tested for their applicability to our problem.

Extraction experiments. Extraction of technetium as the tetraethylammonium hydroxide complex by means of carbon tetrachloride or methyl isobutyl ketone was tested first. The molybdenum was dissolved in 5 ml of a mixture of HNO_3:HCl:H_2O (3:1:3) after which 5 ml of 10 *M* sodium hydroxide were added. To the resulting 1.25 *M* hydroxide solution, 1–5 ml of tetraethylammonium hydroxide was added after which the technetium compound was extracted into carbon tetrachloride or methylisobutyl ketone. More than 99.93% of the ruthenium stayed in the aqueous fraction, but not more than 67% of the technetium was ever extracted. A second extraction scarcely improved matters, and an unextractable species was presumed to be present.

The extraction of technetium with pyridine from aqueous sodium hydroxide was therefore tested. Table I gives the results for extractions of technetium and ruthenium by pyridine, upon dissolution of the molybdenum target in a (3:1) HNO_3:HCl mixture, as a function of the hydroxide molarity. The extraction of technetium was much lower than expected[14], and an appreciable amount of ruthenium was also extracted, in agreement with Gerlit[17]; obviously, the extractions were not influenced appreciably by the alkalinity. In order to establish whether the extractability of the technetium was influenced by the dissolution itself, a set of experiments was made in which the dissolution procedure was kept as constant as possible, after which the solution was brought to 4 *M* sodium hydroxide and the technetium was extracted by pyridine; the percentage extraction of technetium varied from 46% to 99.7%, and a second extraction with a fresh amount of pyridine gave no improvement. Adsorption on the glass did not occur, hence it appeared that there was an unextractable species

TABLE I

TECHNETIUM AND RUTHENIUM EXTRACTION INTO PYRIDINE AS A FUNCTION OF HYDROXIDE MOLARITY

M(NaOH)	*% Extracted by pyridine*	
	Ru	*Tc*
2.7	8	48
3.0	6	44
3.3	7	45
3,5	7.5	49
3.8	8	52
4.0	7	51

of technetium, the amount of which largely depended on small variations in the dissolution procedure. This may be technetium(VI), which is not extractable in pyridine[17], or the technetium may be kept in solution by a reaction with some unknown impurity. The latter explanation is quite possible, for technetium does not occur in nature, so that the solution of technetium is really "carrier-free", and a trace of some inhibitor might account for the irreproducible behaviour.

To avoid this effect, a reagent with very similar behaviour to pertechnetate, *viz.* sodium perchlorate, was added to the dissolution mixture. The molybdenum metal target was dissolved in a (3:1:3) mixture of nitric acid:hydrochloric acid:0.5 *M* sodium perchlorate. After addition of a double volume of 10 *M* sodium hydroxide, which brought the solution to 4 *M* sodium hydroxide, the extraction of technetium by pyridine was repeated. The results are summarized in Table II. This time the extraction of technetium was very reproducible, the distribution constant being 39—the value found by Gerlit[17]. Extractions of ruthenium and molybdenum were less than 0.2% and 0.3%, respectively. As experiments 4a and b show, equilibration with a fresh amount of pyridine or, as experiment 3 shows, with a larger amount of pyridine, did not alter the distribution ratio. All the technetium was therefore in an extractable form, probably because of the protection of the pertechnetate by the perchlorate against the postulated inhibitor.

TABLE II

EXTRACTION OF TECHNETIUM INTO PYRIDINE FROM 4 *M* SODIUM HYDROXIDE SOLUTION CONTAINING 0.06 *M* SODIUM PERCHLORATE

No. of experiment	$V_{pyr}/V_{4\ M\ NaOH}$	$A_{pyr}/A_{4\ M\ NaOH}$	*% Extracted*	K_d
1	1	39	97.5	39
2	1	39	97.5	39
3	10	390	99.75	39
4a	1	40	97.6	40
4b	1	39	99.94	39

Extraction time. Throughout these experiments, shaking times of 1 min were adopted. However, as the total procedure should take less than 1 min, the technetium extraction into pyridine was measured against time. The results showed that a 1-sec extraction was sufficient to reach equilibrium, giving 97.4 ± 0.1% extraction, and there was no difference in percentage extraction over the period 1–30 sec.

It is also time-consuming to wait for the aqueous and organic layers to separate. It was found that neutralization of the acid solute with sodium hydroxide solution brought the solution close to boiling point, and the pyridine layer then separated more quickly. This shortened the waiting period to 3–5 sec.

Procedure. Dissolve the molybdenum target in 5 ml of a warm (3:1:3) mixture of concentrated nitric acid–concentrated hydrochloric acid–0.5 *M* sodium perchlorate. Quickly add the solution to 10 ml of 10 *M* sodium hydroxide. Transfer the hot solution immediately to a separation funnel containing pyridine, and shake for 1 sec. Wait for the layers to separate and collect the aqueous layer.

Discussion

The whole separation procedure can be finished within 20 sec, which is much shorter than the time imposed. If the 97% decontamination is not sufficient, a larger amount of pyridine can be used for the pertechnetate extraction, in which case the pyridine should be heated beforehand in order to minimize the time for the layers to separate.

The distribution constant for pertechnetate is in accordance with the value found for extraction from pure 5 *M* sodium hydroxide. The method proved to be very reproducible.

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ANNOUNCEMENTS

TRENTE-ET-UNIEME CONGRES DU GROUPEMENT POUR L'AVANCEMENT DES METHODES PHYSIQUES D'ANALYSE (G.A.M.S.)

tenu avec la participation de la SOCIETE CHIMIQUE DE FRANCE

Le 31ème Congrès du G.A.M.S. aura lieu à Paris du Lundi 5 au Vendredi 9 Juin 1972. Il sera consacré à des exposés et discussions sur les *Méthodes spectrographiques et chromatographiques d'analyse*. De plus, la journée du vendredi 9 Juin, placée sous l'égide de la Division de Chimie Analytique de la Société Chimique de France, sera consacrée à une mise au point sur diverses méthodes modernes d'analyse. Les séances se tiendront à la Salle d'Iéna, 10, avenue d'Iéna, Paris-16e, où sera présentée simultanément une exposition d'appareils.

Pour tous renseignements complémentaires, envoyer la correspondance à Secrétariat du G.A.M.S. (Congrès), 10, rue du Delta, 75-Paris-9ème, France.

SHORT SUMMER COURSE IN X-RAY POWDER DIFFRACTOMETRY

A one-week short course in modern X-ray powder diffractometry will be offered at the State University of New York at Albany from June 19 to June 23, 1972. The course will be tutorial in nature and will develop the basic theory and practical applications starting from elementary considerations. No previous knowledge or experience are required. Emphasis will be placed on the principles and practice of instrumentation, identification of powder patterns on both qualitative and quantitative basis and practical considerations on the use of the several indices as well as computer retrieval. Equal time will be devoted to lectures and laboratory problem-solving sessions. A suitable amount of time will be set aside for discussion of individual problems. The registration fee is $275.00 payable in advance in American dollars. For further information and to register please communicate with Professor Henry Chessin, State University of New York at Albany, Department of Physics, 1400 Washington Avenue, Albany, N.Y. 12203, U.S.A.

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BOOK REVIEWS

E. Wiberg and E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier Publishing Company, Amsterdam, 1971, xv+785 pp., price Dfl. 290,00 (£33.85).

I doubt very much whether any individual, even those with a direct interest are going to rush out and buy this book. At £33 for 785 pages it is one of the most expensive books of its type I know. Indeed in these days of financial stringency even libraries, particularly in Universities, will think seriously before expending such a large fraction of their resources on a specialised book. Surely publishers must realise that the law of diminishing returns must operate. However, it is clear that quite cynically they set their price level to make a handsome profit on library sales, which generally run from 750–2000 world-wide.

This monograph is an authoritative work by two authors well-known for their expertise in hydride chemistry. The subject matter comprises the hydrides of the alkali and alkaline earth metals, boron, aluminium, gallium, iridium and thallium, silicon, germanium, tin and lead. For each element, known methods of synthesis are critically evaluated and chemical reactions, physical and spectroscopic properties are given. The latter, infrared, n.m.r. etc. are not actually given but references to them are, so that additional library checks are required even to find the Si-H stretching frequency and τ value for SiH_4 for example. Much data and/or references are collected in the 88 tables and it is claimed that approximately 3,800 references are quoted. Literature in 1970 is briefly described in an Appendix. Space could well have been saved by using smaller type for lists of compounds and spectral references as on page 329.

Although the book has been translated commercially from the original German, there appear to be few infelicities in English although some printers' errors are present. The subject index is only 10.5 pages and appears to be less than adequate for a book of this size. There is no author index but references at Chapter ends are listed alphabetically.

The general level of treatment is, of course, very good. There are a few omissions. Thus the reviewer could find no mention of the interaction of NaH with $(CH_3)_2SO$ to give the useful "dimsyl sodium" reagent. Also, notwithstanding the eminence of H. C. Brown, the word hydroboration appears neither in the index or in the text, although some of the reactions are described.

Many people might consider using this book, not for the less useful hydrides such as CsH or SnH_4 but for the common and useful reagents like $LiAlH_4$, NaH, $NaBH_4$ etc. or for borane or carborane chemistry. My own feeling is that they will be better advised to consult books such as Eaton and Lipscomb, Muetterties, Grimes, Mueller, Blackledge and Libowitz, Plesck and Hermanek etc., unless they, or more likely their libraries, are feeling particularly flush. However, for those who can afford it, this book doubtless provides the best general source of information on the hydride compounds of Groups I–IV.

G. Wilkinson (London)

F. Umland, A. Janssen, D. Thierig et G. Wünsch, *Theorie und Praktische Anwendung von Komplexbildnern*, Akademische Verlagsgesellschaft, Frankfurt am Main, 1971, 759 pp., avec 22 figures et 34 tableaux, D.M. 175.—.

Cet ouvrage est le 9ème volume d'une collection éditée par: Prof. Dr. E. Hecht, Vienne, Dr. R. Kaiser, Ludwigshafen, Prof. Dr. E. Pungor, Budapest et Prof. Dr. W. Simon, Zürich, intitulée *Methoden der Analyse in der Chemie*.

L'importance des agents "complexants" n'échappe à aucun chimiste penché sur des problèmes de dosages en relation avec notamment l'analyse de traces d'éléments. C'est dans cette optique que le livre du Dr. F. Umland, Professeur de Chimie analytique minérale à l'Université de Münster et collaborateurs, a été écrit, tout en apportant à l'analyste non spécialisé les notions théoriques et pratiques de base dont il a besoin pour entreprendre un travail en connaissance de cause.

Ainsi, dans un premier chapitre, les auteurs traitent des principes à la base de l'application des agents complexants à l'analyse chimique et présentent la notion de coordinat en relation avec la structure électronique des éléments et commentent les divers complexes formés à partir de ligands uni- ou multidentés en portant un accent particulier sur la formation des chélates. En effet, cette partie théorique, bien que ne se référant pas aux théories modernes de la formation des complexes telle que celle du champ des ligands par exemple, traite néanmoins d'une façon claire et concise:

(*a*) de la stabilité des chélates en introduisant, entre autre, la classification des cations en fonction de leur structure électronique et de leur tendance à la complexation selon Schwarzenbach (1961);

(*b*) de la solubilité des chélates en fonction de la constitution du milieu, de la nature du ligand et des propriétés du solvant;

(*c*) des propriétés optiques des chélates et plus spécialement ce qui touche à l'absorption ainsi qu'à l'émission de fluorescence en corrélation avec la structure du ligand.

Les 400 pages suivantes sont consacrées à la méthodologie du dosage proprement dit, de plus de 50 éléments, par formation de chélates. Les techniques sont groupées de la façon suivante: méthodes gravimétriques, méthodes volumétriques, méthodes photométriques d'absorption et méthodes fluorimétriques.

Pour chaque groupe de méthodes, les auteurs introduisent tout d'abord le principe de celle-ci ainsi que la description générale de l'appareillage utilisé. Ensuite, pour chaque élément, sont mentionnés sous la forme d'une courte revue bibliographique, les divers agents chélatants proposés pour effectuer les dosages. Enfin, une à trois "marche-à-suivre" sont décrites d'une façon suffisamment explicite pour qu'un chimiste ou un laborant entraîné puisse procéder aux dosages sans rencontrer de difficultés majeures. Le choix des méthodes décrites a été fait: en fonction de l'expérience des auteurs et à la vue des avantages signalés par la littérature (sensibilité, sélectivité, précision, interférences, etc.).

L'ouvrage est complété par une abondante liste de références bibliographiques (2456). Il se termine par une revue, sous forme de tableaux, d'une part des diverses techniques de dosage des éléments et, d'autre part, des complexants (plus de 350) et indicateurs les plus courants avec leurs caractéristiques et utilisations.

Bien que général dans sa partie théorique et sans aucun développement mathématique (comme les auteurs l'ont d'ailleurs voulu), ce livre donne une impression sérieuse et nous paraît constituer un manuel de base à recommander à tout étudiant ou chimiste intéressé en la matière et désireux d'utiliser des techniques nouvelles au laboratoire d'analyses chimiques.

Werner Haerdi (Genève)

Chromatographische und mikroskopische Analyse von Drogen, Herausgegeben von E. Stahl, G. Fischer Verlag, Stuttgart, 1970, viii + 195 pp., DM 28.00.

This monograph, a practical supplement to the European Pharmacopeia, is a splendid example of how a subject that could be tedious to learn and dull to read about, is made interesting and is presented very attractively. It begins with a well-illustrated description of the practice of thin-layer chromatography, including the associated thermomicro (t.a.s.) decomposition technique (29 pp.) and a brief treatment of microscopy. The remainder of the text, apart from a few pages concerned with reagent preparation, and an extensive subject index, deals with individual materials that are sources of drugs (opium, liquorice, cinchona bark, etc.). Forty-six main types of material are grouped according to the type of drug (alkaloid, terpene, etc.) they contain. A description of each material contains details of its source, physiological properties, drug content, a microscopic picture of the powdered material, and a procedure for the extraction and t.l.c. separation of the drugs present. In each instance, the chromatograms are reproduced in colour; often, comparison chromatograms for related materials are included.

The book is good value for money, and an English translation would be welcomed by all analysts concerned with the detection of drugs and drug sources.

A. Townshend (Birmingham)

Kazuo Nakamoto, *Infra-red Spectra of Inorganic and Coordination Compounds*, 2nd Edn., J. Wiley and Sons, New York, 1970, xv + 338 pp., price £ 7.00.

The first edition of this book has established it as a central text for those whose interests lie in the vibrational spectra of inorganic and coordination compounds. In this second edition, Part I, which deals with the theory of normal vibrations, has been expanded to include some of the basic theory underlying the Raman effect, crystal spectra and infra-red intensities. Parts II (inorganic compounds) and III (coordination compounds) have been revised to include all the important material published before the end of 1967 as well as some references to later work. These revisions have improved an already excellent text. The price by current standards is not excessive and the book is strongly recommended to those working in this field.

J. K. Brown (Birmingham)

R. J. Abraham, *The Analysis of High-Resolution NMR Spectra*, Elsevier Publishing Company, Amsterdam, 1971, x+324 pp., price Dfl. 95,00 (£11.00).

This book provides a lucid, step by step, account of the procedures currently available for the analysis of high resolution NMR spectra. The early chapters give a concise and well presented summary of the basic theory that could be readily followed by a reader with only a cursory knowledge of NMR spectroscopy. In contrast to many other books on NMR spectroscopy, methods of computer analysis are discussed in detail and the relative accuracy of computer and manual procedures is critically evaluated. The notion of a computer programme as a "black box" is carefully avoided; indeed, the text contains reproduced sections of LAOCOON III output so that the reader is directly in touch with the progress of the analysis. Another attractive feature of this book is that the pitfalls that await the unwary are clearly pointed out (*e.g.* the possibility of obtaining two conjugate solutions in the commonly encountered ABC case). There is a chapter devoted to the method of sub-spectral analysis for the determination of complex spin systems possessing symmetry or containing magnetically equivalent nuclei.

Several problems (with answers) are provided; thus the non-expert reader can become confident in his ability to analyse spectra before embarking on his own problem. Double resonance techniques including noise decoupling and INDOR experiments are briefly discussed, and there is a section on isotopic substitution as an aid to spectral analysis. The book is intended *inter alia* for graduate students; however, the price is so high that most readers will probably have to have recourse to a library copy.

This is an authoritative and well-presented book that should be invaluable to anyone interested in the hand or computer analysis of complex NMR spectra.

W. B. Jennings (Birmingham)

D. Welti, *Infra-red Vapour Spectra*, Heyden/Sadtler, London, xi+211 pp., price £ 8.50.

This book is a collection of vapour phase infra-red spectra (306 in all) run on a small commercial grating spectrophotometer, together with sections on sample handling, frequency correlations, band contour analysis, and the combination of gas chromatography and infra-red spectroscopy. The spectra are classified under the headings alcohols, phenols, carboxylic acids, amines, aldehydes, ketones, esters, lactones, ethers and hydrocarbons. They cover the range 650 to 4000 cm^{-1}, and are clearly presented. The various topics are not discussed extensively, but useful references are given for those who wish to read further. Also, the spectra are supplemented by an index in which a large list of code numbers to vapour spectra found in the major catalogues is given.

The standard of production of this slim book is high and so is the price. The cost will probably dissuade readers from purchasing the book for private use, but it can be recommended for the library, or, preferably, for the laboratory.

J. K. Brown (Birmingham)

VOL. 59 NO. 2 ANALYTICA CHIMICA ACTA APRIL 1972

CONTENTS

Short Communications

(continued on page 4 of cover)

Continued from inside page of cover

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