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Vol. **64**, No. **1**	March 1973	
Vol. **64**, No. **2**	April 1973	
Vol. **64**, No. **3**	May 1973	**(completing Vol. 64)**
Vol. **65**, No. **1**	June 1973	
Vol. **65**, No. **2**	July 1973	**(completing Vol. 65)**
Vol. **66**, No. **1**	August 1973	
Vol. **66**, No. **2**	September 1973	
Vol. **66**, No. **3**	October 1973	**(completing Vol. 66)**
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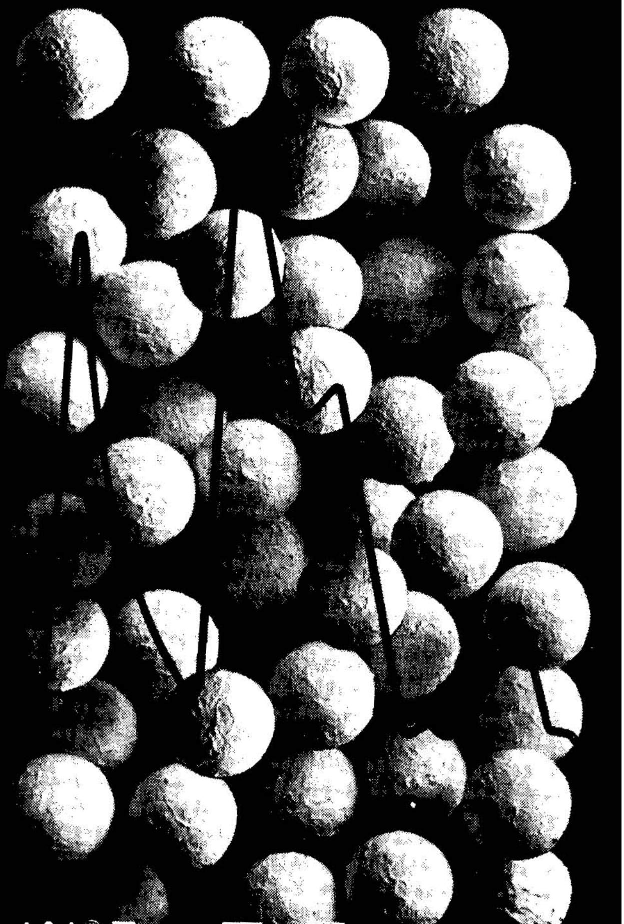

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NONDESTRUCTIVE DETERMINATION OF TRACE IMPURITIES IN IRON BY THERMAL NEUTRON ACTIVATION ANALYSIS WITH LONG-LIVED ISOTOPES

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(Received 6th November 1972)

Nowadays, important scientific research is dedicated to high-purity materials. The chemical and physical properties of such materials being influenced by very small amounts of impurities, it is necessary that accurate quantitative analytical methods are available. For homogeneity control, quite a large number of samples is involved; therefore a simple and fast technique is important. Neutron activation analysis has become a very useful multi-element analytical technique for the determination of trace impurities, especially since the development of Ge(Li) detectors with excellent resolution and sufficiently large efficiency. From a technical point of view, iron may be considered as one of the most important metals. Several papers have already been published dealing with the destructive as well as with the nondestructive neutron activation analysis of iron and steel[1–10].

A simultaneous determination of Cu, Co, Mo, V, Al, Ni and Mn in pure iron and iron ores by means of short-lived isotopes will be published elsewhere by the authors of this paper[11].

In this paper a simultaneous nondestructive determination of Co, Cu, W, As, Ga and Sb in different iron samples, after irradiation for 6 h at a thermal neutron flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1}, is described.

For routine analyses, automation in data collection and reduction is required; this was achieved by using a sample changer and a digital PDP-9 computer.

Nuclear data

In Table I, the nuclear data relevant to the iron matrix are presented. After an irradiation of a few hours in a reactor neutron flux, the isotope ^{56}Mn, produced by the reaction ^{56}Fe(n, p)^{56}Mn gives the most important matrix activity. Because of the small cross-section and isotopic abundance, only a small activity from ^{59}Fe and ^{54}Mn is to be expected. The isotope ^{51}Cr, formed by the reaction ^{54}Fe(n,α)^{51}Cr can only be detected after a chemical separation.

In Fig. 1, a Ge(Li) γ-spectrum of a sample of pure iron, irradiated for 6 h at a thermal neutron flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1} is shown. The decay time was 20 h, and the measuring time 45 min. Peaks of ^{56}Mn, ^{59}Fe and ^{54}Mn matrix activity can be observed. All other peaks in this spectrum are due to impurities in this iron sample. A simultaneous determination of Ga, W, As, Co and Cu is thus possible.

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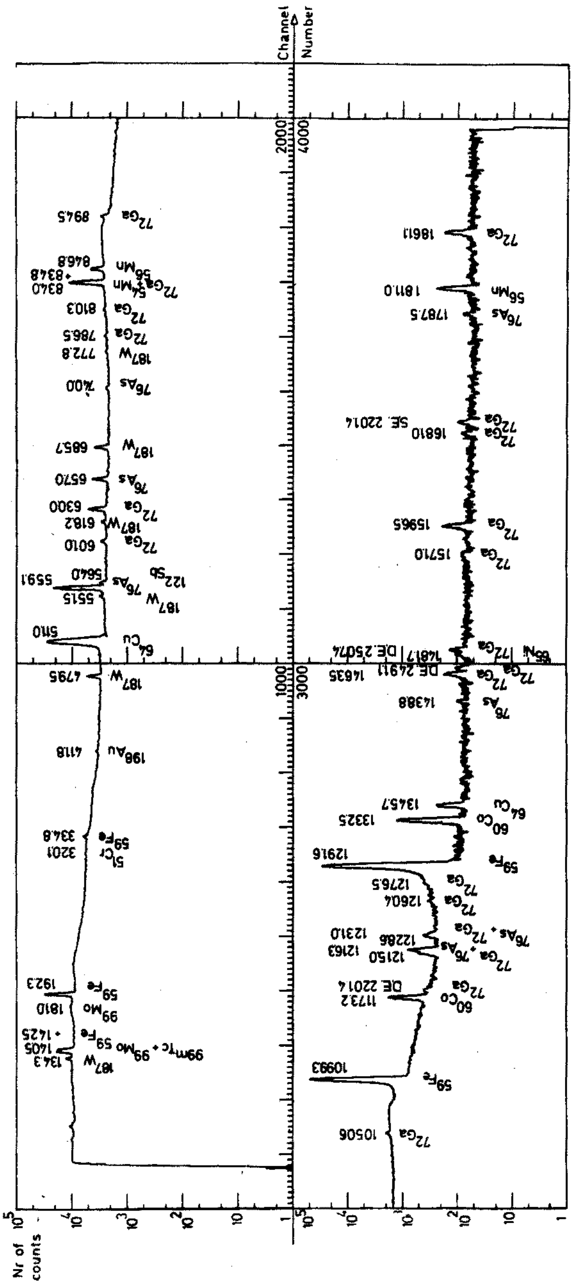

Fig. 1. γ-Spectrum obtained from a thermal neutron irradiated pure iron sample with a 40-cm³ Ge(Li) detector.

TABLE I

NUCLEAR DATA FOR THE ISOTOPES PRODUCED IN THE IRON MATRIX

Isotope	*% Abundance*	*Reaction*	*Produced isotope*	*Cross-section (barn)*[13–15]	*Half-life*	*Decay mode*
^{54}Fe	5.82	(n, γ)	^{55}Fe	2.3	2.7 y	E.C.
		(n, p)	^{54}Mn	$53 \cdot 10^{-3}$	313 d	E.C., γ
		(n, α)	^{51}Cr	$0.74 \cdot 10^{-3}$	27.8 d	E.C., γ
		(n, 2n)	^{53}Fe	$0.0032 \cdot 10^{-3}$	8.4 m	β^+, E.C., γ
^{56}Fe	91.66	(n, γ)	^{57}Fe	2.6	Stable	
		(n, p)	^{56}Mn	$0.87 \cdot 10^{-3}$	2.582 h	β^-, γ
		(n, α)	^{53}Cr	$0.35 \cdot 10^{-3}$	Stable	
		(n, 2n)	^{55}Fe	$0.07 \cdot 10^{-3}$	2.7 y	E.C.
^{57}Fe	2.19	(n, γ)	^{58}Fe	2.5	Stable	
		(n, p)	^{57}Mn	$0.4 \cdot 10^{-3}$	1.7 m	β^-, γ
		(n, α)	^{54}Cr	$3.5 \cdot 10^{-3}$	Stable	
		(n, 2n)	^{56}Fe	$3.0 \cdot 10^{-3}$	Stable	
^{58}Fe	0.33	(n, γ)	^{59}Fe	1.2	45 d	β^-, γ
		(n, p)	^{58}Mn	$0.01 \cdot 10^{-3}$	1.1 m	β^-, γ
		(n, α)	^{55}Cr	$0.01 \cdot 10^{-3}$	3.53 m	β^-, γ
		(n, 2n)	^{57}Fe	$0.2 \cdot 10^{-3}$	Stable	

Use of an internal standard

Experiments[12] have shown that in the reactor used, flux gradients up to 17% over the length of the irradiation containers occur. As several 1.5-g samples with a significant volume are irradiated simultaneously, in the same container, these flux gradients may cause considerable errors.

Moreover, errors can be introduced if the source-to-detector geometry of samples and standards during the measurements is not exactly the same, especially if the distance to the detector is rather small.

These two effects can be easily corrected by using the ^{59}Fe matrix activity as an internal standard.

The total impurities in both standard and sample ($<0.2\%$) are practically very low, hence the specific activity induced in the iron matrix can be used as a flux monitor. At the same time small differences in the source-to-detector geometry between samples and standards during the counting time can be taken into account. To a certain extent, differences in neutron shielding and γ-ray attenuation effects caused by differences in density between standards and samples are also compensated for.

PREPARATION OF MULTI-ELEMENT STANDARDS

When dealing with a nondestructive method it is desirable to have standards of the same geometry as the samples. It was decided to prepare a powder containing all standards, from which pellets of the same geometry as the samples could be pressed.

For reason of internal standardization, iron powder was chosen as a standard matrix. Very pure carbonyl iron powder is commercially available. A preliminary analysis of the impurities present in the carbonyl iron powder used in this work, showed an important amount of molybdenum only. Results for the most important impurities, determined by activation analysis, are listed in Table II.

TABLE II

IMPURITIES IN CARBONYL IRON

(Errors are standard deviations on the mean in p.p.m.)

Element	*Concentration (p.p.m.)*
Mo	55.9 ± 0.4
W	1.78 ± 0.02
Cu	0.75 ± 0.03
Co	< 0.05
As	< 0.002
Ga	< 0.1
Ni	8 ± 2
Al	1.65 ± 0.14
V	< 0.01
Mn	0.35 ± 0.04

TABLE III

HOMOGENEITY OF STANDARDS

Isotope		*Standards (conc. in p.p.m.)*						*Average* $\pm s_r$	*s expected*
Name	*Energy (keV)*	*2*	*3*	*4*	*5*	*6*	*7*		
^{72}Ga	601.1	58.0	58.7	60.5	57.7	60.3	58.6	59.0 ± 1.2	3.5
	630.1	59.8	59.1	58.0	60.2	59.3	58.2	59.1 ± 0.9	0.9
	834.1	59.2	60.3	59.1	—	60.0	59.7	59.7 ± 0.5	0.4
	1050.6	57.1	58.6	60.5	—	60.3	65.0	60.3 ± 2.9	3.1
	1596.2	57.7	56.5	50.1	—	59.5	60.3	56.8 ± 4.0	3.5
	1860.4	58.9	54.0	56.9	—	58.6	58.4	57.4 ± 2.0	3.8
^{187}W	134.3	18.0	18.1	18.5	18.0	18.2	18.3	18.2 ± 0.2	0.3
	479.3	18.2	18.0	17.9	18.0	17.8	18.0	18.0 ± 0.2	0.2
	551.4	19.1	18.7	18.5	17.5	18.0	17.9	18.3 ± 0.6	0.8
	618.1	19.4	18.8	17.8	17.9	18.3	18.2	18.4 ± 0.6	0.8
	685.7	18.0	18.0	17.9	18.1	17.9	17.9	18.0 ± 0.2	0.2
	772.9	16.0	17.9	16.5	17.5	17.9	16.2	17.0 ± 0.9	1.0
^{76}As	559.2	4.32	4.23	4.23	4.35	4.30	4.27	4.28 ± 0.05	0.1
	657.0	4.35	5.31	5.58	5.02	4.42	5.16	4.97 ± 0.49	0.7
^{60}Co	1173.1	222	261	229	—	254	233	240 ± 17	8.4
	1332.4	264	275	257	—	260	262	264 ± 7	8.7

In order to prepare suitable standards, known amounts of the elements to be determined were added to 15 g of the powder. From a stock solution of Co, Cu, Sb and Ga, dissolved in 3 *M* nitric acid, and of As and W dissolved in 3 *M* ammonia solution, 100-μl aliquots were pipetted on the powder. Care had to be taken to deposit the entire volume onto the powder, in order to avoid contact of the solution with the walls of the vessel. The 100-μl aliquots contained approximately 5000 μg of Co, 1000 μg of Cu, 1000 μg of Sb, 200 μg of Ga, 200 μg of As and 100 μg of W.

After drying for 10 h at 120°, the mixture was ground in an agate mortar and homogenized for 3 h in a "Turbula" mixer.

The homogeneity of the standard powder and the reproducibility of the preparation method was tested. In the first experiment Ga, W, Co and As were added as described to 15 g of carbonyl iron powder; after drying and homogenizing, 7 pellets ($\varnothing = 6$ mm, height $= 6$ mm) of 1.2 g each were pressed at 140 kg cm^{-2}. The obtained density was 6.2. They were irradiated for 6 h at a flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1}. After a decay time of 24 h the pellets were measured with a 40-cm^3 Ge(Li) detector. The amounts of Ga, W, As and Co were calculated, with one of the pellets acting as a reference standard. Table III shows the results of this homogeneity test. As can be seen the homogeneity can be considered as sufficient, for the standard deviation is close to that expected from counting statistics only.

In another experiment the reproducibility of this standard preparation was tested. Four independent preparations of standard powder for the same elements Ga, W, As and Co were carried out. From each preparation, two pellets were analysed, one pellet of one preparation serving as a reference standard. Table IV shows the results of this experiment. When the most intense photopeaks were used for the concentration calculations, the obtained precisions for Ga, As and Co were also close to those expected from counting statistics. The results for W showed a larger standard deviation than expected proving that the reproducibility of the standard preparation could not be completely trusted. Therefore, for the analysis of the samples, the average of three or four standard pellets from different preparations was used as a reference.

In order to know the exact concentration of the elements in the standard, corrections had to be made to account for the impurities present in the carbonyl iron powder. Only for tungsten and copper were these corrections necessary.

EXPERIMENTAL

Preparation of the samples

Pure iron samples were obtained from an iron bar of 90 kg with a length of 6.8 m which was part of a batch of 200 kg, prepared for the Verein Deutscher Eisenhüttenleute. Four discs of 43.5 mm diameter and 30 mm thickness, cut from that bar at different positions were available. For the nondestructive analysis, small cylindrical samples of 6 mm diameter and 6 mm length were machined out of these discs. The weight of the samples was *ca.* 1.45 g.

Four different kinds of pure iron, in the form of turnings, prepared by Krupp, Essen were also available. From these turnings pellets of 6 mm length and 6 mm diameter were pressed at 140 kg cm^{-2}. The weight of the pellets was *ca.* 1.30 g.

TABLE IV

REPRODUCIBILITY OF THE STANDARD PREPARATION METHOD

Isotope	*Energy (keV)*	*Concentration (p.p.m.)*								*Average*	s_r(%)	*Expected* s_r(%)
		1st preparation		*2nd preparation*		*3rd preparation*		*4th preparation*				
^{72}Ga	601.1	33.1	35.1	33.7	33.5	35.2	35.9	32.7	34.4	34.2	3.3	4.6
	630.1	33.1	33.6	33.4	35.3	34.1	34.8	33.8	33.2	33.9	2.3	1.4
	834.1	33.1	33.4	34.6	34.4	34.3	34.4	33.7	34.3	34.0	1.5	0.5
	1050.6	33.1	37.4	38.5	36.5	36.9	39.7	38.5	35.0	36.9	5.7	5.3
	1596.2	33.1	31.5	35.2	32.9	36.1	35.6	37.4	34.1	34.5	5.6	4.9
	1860.4	33.1	29.7	33.0	32.5	33.0	34.8	34.2	34.7	33.1	4.9	5.1
^{187}W	134.3	10.1	10.3	10.7	10.4	9.21	9.30	11.2	11.1	10.3	7.2	0.2
	479.3	10.1	10.5	10.5	10.7	9.19	9.18	11.3	11.2	10.3	7.8	0.7
	551.4	10.1	—	11.3	10.6	8.96	9.09	11.7	11.9	10.5	11.4	3.6
	618.1	10.1	8.7	9.10	8.89	7.57	7.74	9.57	9.67	8.9	10.1	2.9
	685.7	10.1	10.2	10.5	10.5	8.98	8.87	11.2	11.2	10.2	7.6	0.8
	772.9	10.1	—	10.7	10.8	9.23	8.60	11.1	11.7	10.3	10.6	4.6
^{76}As	559.2	2.42	2.25	2.34	2.46	2.45	2.45	2.44	2.45	2.41	3.1	2.2
	657.0	2.42	1.99	2.09	2.63	2.57	2.54	2.51	2.77	2.44	11	15
	1215.8	2.42	2.21	2.12	1.79	2.40	2.08	1.85	1.98	2.11	11	11
	1228.8	2.42	2.45	2.38	1.36	2.09	1.89	1.82	1.86	2.03	19	12
^{60}Co	1173.1	149	146	153	153	149	149	156	136	149	4.1	3.5
	1332.4	149	144	148	149	152	152	148	148	149	2.6	2.9

Irradiation conditions

All irradiations were carried out in the Thetis reactor of the University of Ghent. In a typical analysis 4 standard pellets and 4 samples were irradiated during 6 h in a rabbit tube with a thermal flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1}. The isotopes used for the determination of trace impurities, together with their half-lives, the energies of the peaks used, parent abundances, cross-sections and specific activities obtained after a 6-h irradiation with a flux of $5 \cdot 10^{11}$ n cm^{-2} s^{-1} are given in Table V. The corresponding calculated matrix activities are also listed. Specific activities are given in dis μg^{-1} s^{-1} for the impurities and in dis g^{-1} s^{-1} for the activities due to the matrix.

TABLE V

NUCLEAR DATA INCLUDING SENSITIVITIES FOR THE ISOTOPES USED IN THE ANALYSIS

Isotope	*% Abundance*	*Reaction*	*Produced isotope*	*Cross-section*	*Half-life*	*γ-Rays used*	*Spec. activity (dis μg^{-1} s^{-1}; *dis g^{-1} s^{-1})*
^{59}Co	100	(n, γ)	^{60}Co	18+19	5.258 y	1173.1 1332.4	17
^{63}Cu	69.17	(n, γ)	^{64}Cu	4.7	12.75 h	511.0 1345.5	4270
^{71}Ga	39.84	(n, γ)	^{72}Ga	4.8	14.1 h	630.1	2100
^{75}As	100	(n, γ)	^{76}As	4.3	26.4 h	559.2 657.0	2510
^{121}Sb	57.25	(n, γ)	^{122}Sb	0.06	2.74 d	564.0	5.2
^{186}W	28.41	(n, γ)	^{187}W	36	23.9 h	479.3 685.7	2670
^{54}Fe	5.42	(n, p)	^{54}Mn	$53 \cdot 10^{-3}$	313 d		1710*
^{54}Fe	5.42	(n, α)	^{51}Cr	$0.74 \cdot 10^{-3}$	27.8 d		4530*
^{56}Fe	91.66	(n, p)	^{56}Mn	$0.87 \cdot 10^{-3}$	2.582 h		686000*
^{58}Fe	0.33	(n, γ)	^{59}Fe	1.2	45 d		81700*

Data collection

As ^{56}Mn gives a considerable activity immediately after irradiation, a cooling period of 15 h was introduced. All spectra were measured with a 40-cm^3 Ge(Li) detector (resolution 2.3 keV and peak-to-Compton ratio 25 for the 1332-keV γ-ray of ^{60}Co), connected to an Intertechnique DIDAC 4000-channel analyser. The measuring time was 45 min. As a complete analysis cycle of 4 standards and 4 samples took about 7 h, an automatic sample changer was used.

After each measurement the γ-spectrum was stored on magnetic tape, by means of an Intertechnique RG 23 tape recorder. Afterwards the spectra could be transferred to a PDP-9 computer for further interpretation. A block scheme of the interconnections of counting equipment, recording devices and the computer is presented in Fig. 2.

Data interpretation

The concentration of the impurities in the samples was calculated, by means

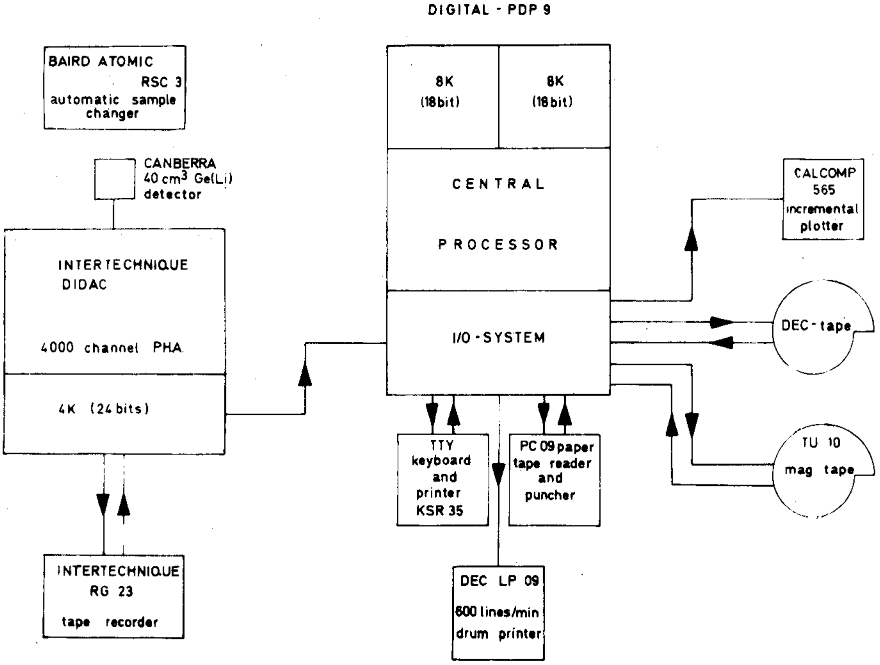

Fig. 2. Block scheme of the interconnections of counting equipment, recording devices and computer.

of the PDP-9 computer, with the aid of the quantitative neutron activation analysis program AKTAN. A detailed description of this program and its application to the analysis of high-purity iron has been published[16]. After all the necessary information such as calibration parameters, name and energy of the isotopes, half-life of the isotopes, number of channels of each spectrum, resolution of the detector, counting time, decay time, irradiation time, weight of sample and standard and internal standard normalization factor has been furnished, AKTAN automatically calculates the concentration of the impurities or the upper limits of the elements involved.

An example of the results obtained for one sample is given in Table VI. As can be seen, the concentrations are calculated from several peaks. For each peak the obtained weight of impurity and concentration in p.p.m. are given. AKTAN also calculates the % standard deviation, based on counting statistics and the detection limit for every peak.

RESULTS AND DISCUSSION

In Table VII the results obtained for analyses of the high-purity iron, are listed. Average concentration, standard deviation and standard deviation expected from counting statistics are given. Each value is the average of the results obtained with three different standards as a reference.

In principle every observable peak can be used for the determination of the corresponding element. However, as can be seen in Fig. 1, a judicious choice of the most appropriate peak may contribute much to the obtainable accuracy and preci-

TABLE VI

TYPICAL COMPUTER OUTPUT OF FINAL ANALYSIS RESULTS FOR ONE SAMPLE

Element name	*Weight (μg)*	*Concentration (p.p.m.)*	*s_r (%)*	*Det. limit (μg)*	*Energy (keV)*	*Counts per half-life*
W	0.1985E+01	0.1140E+01	9.37	0.4098E+00	133.58	0.171E+06
W	0.2168E+01	0.1245E+01	4.31	0.1594E+00	479.12	0.152E+06
Cu	0.7067E+02	0.4058E+02	0.45	0.4799E+00	510.61	0.222E+07
W	0.1529E+01	0.8781E+00	26.66	0.5942E+00	551.10	0.211E+05
As	0.1530E+02	0.8785E+01	0.99	0.1588E+00	558.82	0.134E+07
Ga	0.1003E+02	0.5758E+01	13.19	0.2452E+01	600.67	0.277E+05
W	0.2575E+01	0.1479E+01	12.76	0.7657E+00	617.88	0.391E+05
Ga	0.1112E+02	0.6387E+01	3.37	0.6356E+00	629.71	0.122E+06
As	0.1477E+02	0.8483E+01	5.54	0.1137E+01	656.70	0.154E+06
W	0.2030E+01	0.1166E+01	3.85	0.1539E+00	685.44	0.132E+06
W	0.2181E+01	0.1252E+01	28.49	0.1203E+01	772.57	0.188E+05
Ga	0.1204E+02	0.6911E+01	1.21	0.2493E+00	833.92	0.420E+06
Ga	0.1190E+02	0.6831E+01	16.73	0.4227E+01	1050.61	0.214E+05
Co	0.1389E+03	0.7978E+02	2.38	0.5931E+01	1173.16	0.202E+09
As	0.1463E+02	0.8398E+01	8.23	0.1905E+01	1216.05	0.363E+05
As	0.1682E+02	0.9656E+01	20.68	0.4875E+01	1228.85	0.179E+05
Co	0.1417E+03	0.8138E+02	1.83	0.3542E+01	1332.45	0.182E+09
Cu	0.8423E+02	0.4837E+02	10.30	0.1115E+02	1345.82	0.118E+05
Ga	0.9791E+01	0.5622E+01	10.03	0.1765E+01	1596.80	0.822E+04
Ga	0.1156E+02	0.6639E+01	9.10	0.1949E+01	1860.97	0.926E+04

TABLE VII

DETERMINATION OF W, As, Ga, Co AND Cu IN HIGH-PURITY IRON

Element	*Energy used (keV)*	*Sample 1*	*Sample 2*	*Sample 3*	*Sample 4*	*Average*	*s_r (%)*	*Expected s_r (%)*
W	134.3	1.28	1.55	1.18	1.27	1.32	12.1	9.4
	479.5	1.27	1.34	1.35	1.40	1.34	4.0	4.4
	685.7	1.34	1.28	1.30	1.31	1.31	1.9	3.9
As	559.1	8.55	8.77	8.77	8.80	8.72	1.3	1.0
	657.0	7.95	8.78	8.03	8.79	8.39	5.5	5.9
Ga	630.0	6.06	6.24	6.57	6.23	6.27	3.4	3.4
	834.0	6.52	6.78	6.65	6.96	6.73	2.8	1.4
Co	1173.2	76.1	79.5	77.4	80.8	78.5	2.7	2.7
	1332.5	79.5	81.8	80.0	81.2	80.6	1.3	2.0
Cu	511.0	41.0	39.6	42.1	41.2	41.0	2.5	0.5
	1345.7	48.1	45.8	47.6	44.4	46.5	3.7	10.2

sion. Although the most intense peaks will guarantee the highest precision, some of them should be avoided, because there are interferences from peaks of other isotopes of a different chemical element, resulting in systematic errors. On the other hand, for a single isotope not all the peaks that are free from interference should be used to calculate concentrations averaged over all peaks. As can be seen in Table IV the smallest peaks may have poor precision.

The determination of tungsten was based on the peaks from the γ-rays at 479.5 keV and 685.7 keV. For copper, the peak from the 511.0-keV γ-ray could be used; as the amount of copper in the samples (40 p.p.m.) led to a relatively large activity, the contribution of the 511.0-keV γ-rays arising from internal annihilation radiation from high-energy γ-rays, could be neglected. Moreover, as both sample and standard spectra were quite similar in composition, this contribution was similar and thus would not introduce an appreciable error. For the determination of gallium the most intense peak at 834.0 keV could not be used because of the interference of the 834.8-keV γ-rays of the isotope ^{54}Mn which is produced by an (n, p) reaction in the iron matrix. Therefore the results obtained by means of the peak from the 630.0-keV γ-rays were preferred. The peaks at 1173.2 and 1332.5 keV of ^{60}Co could both be used for the determination of cobalt. For arsenic, besides the 559.1-keV peak, the peak at 657.0 keV also gave good quantitative information.

The most striking feature of Table VII is the excellent agreement between the expected standard deviation, based on pure counting statistics, and the observed standard deviation derived from the analysis of several samples. Although this may be partly due to the fact that up to three standards were used for every irradiation, it should be mainly explained by the use of the activity induced in the iron matrix as an internal flux monitor during irradiation and as a γ-ray attenuation monitor during counting. In this way the flux gradients of 5–15% that are known to exist between standards and samples during the irradiation, do not contribute substantially to the observed error.

Four different kinds of pure iron, available in the form of turnings, were analysed by the same method. The results are given in Table VIII. The values listed are averages of two determinations. The concentration of antimony in these iron samples was high enough to allow a nondestructive determination based on the 564.0-keV peak of ^{122}Sb. Because the total impurity concentration was relatively high, the sensitivity for each individual element was less favourable compared to the high-purity iron. Therefore cobalt was determined from a second measurement after decay of ^{76}As, ^{72}Ga, ^{64}Cu, ^{122}Sb and ^{187}W in order to obtain better counting statistics.

TABLE VIII

ANALYSIS OF FOUR SAMPLES OF IRON TURNINGS

Code	*As*	*Ga*	*W*	*Sb*	*Cu*	*Co*[a]	*Co*[b]
V 2444	18.2±1.0	13.0±0.2	0.77±0.06	2.50±0.12	37.4±0.12	43.3±0.8	42±2
Co 12	252±12	15.7±0.2	0.52±0.08	42.3±0.8	671±12	276±2	250±10
ARMCO							
Co 13	129±6	51.2±4.2	19.9±0.2	55.3±2.2	201±20	98.1±0.6	93±5
Co 14	33.1±1.8	18.2±0.2	6.20±0.08	18.2±0.4	39.7±0.6	36.5±0.8	35±4

[a] Neutron activation analyis.

[b] Average of colorimetric analyis by eight independent laboratories.

For pure iron, manganese could also be determined, if the samples and standards were measured at a relatively short time after the end of the irradiation. However, it was more advantageous to let manganese decay almost completely in order to increase the sensitivity of the other elements. Manganese itself can be determined after a shorter irradiation with much better precision.

In the case of the pure iron, cobalt and copper were also determined nondestructively together with Mo, V, Al, Mn and Ni with the aid of short-lived isotopes[11]. A destructive analysis, including group separations as well as complete isolation of certain elements, among which were cobalt and copper, was also carried out. The results (Table IX) show that for the three methods based on different techniques and standards, a very satisfactory agreement was obtained. Whenever possible the nondestructive method should be preferred, since it is not only appreciably faster than destructive analysis techniques, but gives a greater freedom from systematic errors and offers improved precision, especially if an internal standard is used.

TABLE IX

COMPARISON OF DIFFERENT ANALYTICAL TECHNIQUES FOR THE ANALYSIS OF HIGH PURITY IRON

(Errors are standard deviations on the mean in p.p.m.)

Element	*Concentration ((p.p.m.)*		
	Nondestructive long lived	*Nondestructive short lived*	*Destructive*
Cobalt	79.2±0.6	78.3±0.6	80.3±0.5
Copper	41.0±0.6	42.9±0.6	40.1±0.6

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SUMMARY

A method is proposed for the instrumental determination of Co, Cu, W, As, Ga and Sb in a pure iron matrix. Semiconductor detectors with high resolving power, automatic data collection and completely computerized data interpretation have been used. A method of preparing and testing composite multi-element standards is described in detail.

RÉSUMÉ

Une méthode d'analyse non-destructive est proposée pour le dosage d'impuretés, en traces, dans une matrice de fer pur. On procède par activation neutronique thermique, en utilisant des détecteurs semiconducteurs à haut pouvoir de résolution, avec interprétation complètement automatique des résultats. On décrit en détail la préparation d'étalons multi-éléments.

ZUSAMMENFASSUNG

Es wird eine Methode für die instrumentelle Bestimmung von Co, Cu, W, As, Ga und Sb in einer reinen Eisen-Matrix vorgeschlagen. Halbleiterdetektoren mit hohem Auflösungsvermögen, automatische Zusammenführung der Zahlenergebnisse und deren Interpretation unter ausschliesslicher Verwendung eines Computers wurden angewendet. Eine Methode zur Herstellung und Prüfung von zusammengesetzten Standardproben mit mehreren Elementen wird ausführlich beschrieben.

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THE FLUORIMETRIC DETERMINATION OF MERCURY

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In a recent investigation of the use of thiamine for the fluorimetric determination of phosphate[1], mercury(II) was found to react with thiamine to give high fluorescence; this reaction, as far as we know, is the first reported instance of mercury-induced fluorescence. The present paper describes the use of thiamine for the fluorimetric determination of mercury; inorganic mercury(II) (0.1–5 μg or 10–500 ng ml^{-1}) is readily determined in solutions which have a relatively low salt concentration (< 0.02 M). Where digestion with acids is necessary for sample preparation (*e.g.* organics), samples containing 10–500 μg of mercury are required because the high salt concentration resulting from neutralization must be decreased by dilution.

EXPERIMENTAL

Apparatus, reagents, solutions

All fluorimetric measurements were made with an Aminco-Bowman spectrofluorimeter in 1-cm quartz cells using a xenon arc source. The instrument was standardized by a 1-p.p.m. solution of quinine sulphate (λ_{ex} 350 nm; λ_{em} 450 nm). Slit widths for all measurements were 1, 4, 5, 5, 4, 3, 5 mm for slit No. 1, 2, 3, 4, 5, 6, 7, respectively.

Stock solutions of 0.01 M mercury(II) chloride (Merck) and 0.01 M thiamine chloride hydrochloride (Aldrich) were prepared. The mercury(II) solution was standardized by EDTA substitution titration[2]. Solutions of the desired concentration were freshly prepared daily by dilution of the stock solutions.

The borate buffer (pH 7.7) was prepared by mixing 47 ml of 0.1 M hydrochloric acid with 53 ml of 0.05 M borax.

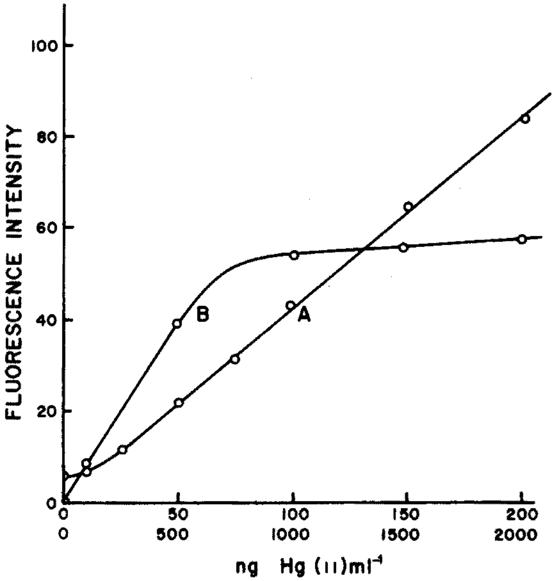
Procedure

To 2 ml of buffer in a 10-ml volumetric flask add several milliliters of approximately neutral unknown solution (containing 0.1–5 μg of mercury), 1 ml of $3 \cdot 10^{-5}$ M reagent and make up to volume with twice-distilled water; the resulting solution should be less than 0.02 M in foreign salts. Measure the fluorescence intensity at 440 nm, after 1 h or more; the excitation wavelength is 375 nm. A blank should be run concurrently. A typical calibration curve is shown in Fig. 1 (curve A).

Factors affecting fluorescence

The determination is based on the oxidative reaction of mercury(II) on thiamine to produce highly fluorescent thiochrome; mercury must, therefore, be present in solution in the divalent state. Mercury(I) solutions give a fluorescence intensity of about one-half that obtained for the same concentration of mercury(II) and organomercury compounds can only be successfully analyzed after destruction of organic matter and conversion to inorganic mercury(II).

The ratio of sample to blank intensity is essentially constant over the pH range 7–8 but decreases rapidly at both lower and higher pH values; no differences were observed, for example, between blank and sample at pH 4.5 and at pH 11.



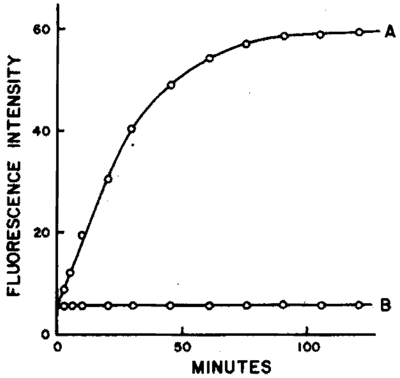


Fig. 1. Fluorescence–concentration dependence. (A) 0–200 ng ml^{-1} at instrumental settings for meter multiplier (MM) and sensitivity (S) of 0.03 and 0.0, respectively; (B) 0–2000 ng ml^{-1} at MM 0.3 and S 0.0.

Fig. 2. Fluorescence–time dependence (MM 0.03 and S 0.0). (A) 100 ng Hg(II) ml^{-1}; (B) blank.

The fluorescence intensity is both time- and reagent-concentration-dependent. Highest sensitivity is obtained at a reagent concentration of $3 \cdot 10^{-6}$ *M* after standing for *ca.* 1 h (Fig. 2). Constant fluorescent intensity can be obtained for higher reagent concentrations within a few minutes but a lower sensitivity is achieved.

Heating increases the reaction rate so that solutions heated to 90° for 10 min give essentially the same reading, after cooling, as solutions allowed to stand at room temperature for 1 h before measurement; the reading for the blank does not change appreciably on heating.

RESULTS AND DISCUSSION

The fluorescence intensity is a linear function of mercury concentration from 10 to 200 ng ml^{-1}; the curve does not pass through the origin because of some background fluorescence. At higher mercury concentrations, where lower instrument sensitivity is necessary, there is no measurable background fluorescence and a straight line is obtained up to 500 ng Hg ml^{-1} (Fig. 1B) under the procedural conditions; a linear relationship between fluorescence intensity and concentration is obtained at considerably higher mercury levels if the reagent concentration is increased. The relative standard deviation on the analysis of 50 ng Hg ml^{-1} (7 determ.) was 4.1%; for 100 ng Hg ml^{-1} (10 determ.), it was 3.2%.

Interferences

Mercury(II) (50 ng ml^{-1}; $2.5 \cdot 10^{-6}$ mmole) was successfully determined in the presence of a 10,000-fold (molar) amount of nickel(II), cobalt(II) or zinc(II); a 1000-fold amount of copper(II), cadmium(II), manganese(II) or aluminum(III); or a 100-fold amount of iron(II) or iron(III). Similarly, 100,000-fold amounts of the sodium or potassium salts of acetate, chloride, citrate, sulfate or tartrate did not interfere. A 10,000-fold amount of fluoride, nitrate, perchlorate or phosphate, and a 1000-fold amount of bromide and thiocyanate could be tolerated; the fluorescence was quenched by equivalent amounts of cyanide, iodide, sulphide or EDTA.

Applications of the method

For samples which require acid treatment before the determination of mercury (*e.g.* in the destruction of organic material), sample sizes must be taken to provide 10–500 μg of mercury. Salt concentrations in excess of 0.02 *M* decrease the fluorescence intensity and it is therefore necessary to dilute the digested solution, ordinarily by about two orders of magnitude, to obtain good results. The digestion technique recommended by Nelson *et al.*[3] was applied to water samples and to organomercurials and was found to be very satisfactory; the method consists of boiling the sample with a mixture of concentrated sulphuric and nitric acids in an Erlenmeyer flask fitted with a short-stemmed funnel, care being taken to prevent charring and resultant mercury loss through carbon reduction.

Tap water samples (25 ml), for example, were spiked with mercury(II) chloride and were digested with 1 ml of concentrated sulphuric acid and 1 ml of concentrated nitric acid. After digestion the solutions were neutralized to pH 7.5–8 with 50% sodium hydroxide (some borax was added to provide buffering) and were then made up to the original 25-ml volume. An aliquot of this solution was diluted 100 times to decrease the salt concentration to less than 0.02 *M* and the regular procedure with thiamine was applied. The relative error of determination was less than 5%.

Samples (5 mg) of di-*p*-tolylmercury (Eastman) were similarly digested with acids and were successfully analyzed for mercury with thiamine. The precision was excellent and the relative error of 6% was satisfactory, considering the unknown purity of the sample.

Excellent results were also obtained with a simple fluorimeter (Turner Model 110, primary filter 7-60 and secondary filter 2A).

This work was supported by grants from the National Research Council and Defence Research Board.

SUMMARY

Mercury(II) in solutions less than 0.02 *M* in foreign salts is selectively and

simply determined at the 10–500 ng ml^{-1} level by measuring the fluorescence produced on reaction with thiamine. Sample sizes to provide 10 μg or more of mercury must be taken for samples which require acid digestion before analysis (*e.g.* organics), because of the need for dilution to avoid salt interference.

RÉSUMÉ

Une méthode est proposée pour le dosage sélectif du mercure(II), en quantités allant de 10 à 500 ng ml^{-1}, dans des solutions dont la teneur en sels étragers est inférieure à 0.02 *M*. On procède par mesure de la fluorescence produite par la thiamine. Lorsqu'un traitement préalable à l'acide est nécessaire, on prélèvera des volumes d'échantillon contenant au moins 10 μg de mercure; car il faudra procéder à une dilution avant de faire les mesures de fluorescence, pour éviter une interférence de sel.

ZUSAMMENFASSUNG

Quecksilber(II) in Lösungen mit weniger als 0.02 *M* Fremdsalzen wird im Bereich 10–500 ng ml^{-1} selektiv und einfach bestimmt, indem die nach Reaktion mit Thiamin hervorgerufene Fluoreszenz gemessen wird. Proben, die eine Säurebehandlung vor der Analyse erfordern (z.B. organische Proben), müssen 10 μg oder mehr Quecksilber enthalten, weil zur Vermeidung von Störungen durch Salze eine Verdünnung notwendig ist.

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EXTRACTION–SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF BISMUTH IN LEAD, COPPER AND NICKEL METALS, AND IN COPPER-BASE ALLOYS WITH TRI-*n*-OCTYLAMINE

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In the past, traces of bismuth in lead, copper and nickel metals have generally been determined by polarography[1–5] or colorimetry[1,6,7]. These methods are subjected to interferences from matrix elements or from numerous impurities in the metals and require a prior separation by coprecipitation[1,3,4,6,7] or solvent extraction[2,5]; in addition, it is necessary to take very large amounts (10–50 g) of sample, because of the relatively low sensitivities of the methods, and the low bismuth contents in the metals. A rapid, simple and sensitive method for the determination of bismuth in the above materials is therefore considered to be desirable.

Recently, Burke[8] has reported a sensitive atomic absorption spectrometric method in conjunction with a coprecipitation technique and determined trace amounts (1 p.p.m. levels or more) of bismuth in nickel, but this method is relatively time-consuming. The present authors[9] have studied a rapid and sensitive atomic absorption method in conjunction with a solvent extraction technique and determined trace amounts (1 p.p.m. levels or more) of bismuth in the above materials. The present paper describes a spectrophotometric method for the determination of traces of bismuth in lead, copper, nickel metals and copper-base alloys. The proposed method involves the extraction of bismuth with tri-*n*-octylamine in benzene in the presence of hydrobromic acid, and measuring the color intensity of a bromo-complex of bismuth extracted. The method is simple, rapid and sensitive, and its selectivity for bismuth is good. The optimal conditions for the extraction and determination of bismuth are discussed.

EXPERIMENTAL

Apparatus

The spectrophotometric measurements were made on a Hitachi 139 spectrophotometer in 1-cm cells. An Iwaki KM shaker was used for the extraction of bismuth.

Reagents

All chemicals used were of JIS-special grade.

Tri-n-octylamine solution. Dissolve tri-*n*-octylamine (Wako Pure Chemical Industries, Ltd.) in benzene, chloroform, or carbon tetrachloride.

Wash solution A. Dissolve 170 g of sodium nitrate in water. Add 11.6 ml of hydrobromic acid and dilute to 1 l with water; this solution is 2 *M* with respect to sodium nitrate and 0.1 *M* with respect to hydrobromic acid.

Standard bismuth solution. Dissolve 0.100 g of high-purity bismuth metal in 5 ml of nitric acid (1+1). Make basic with ammonia, filter the precipitated bismuth hydroxide and wash the precipitate with diluted ammonia. Dissolve the precipitate with 30 ml of 4 *M* hydrobromic acid and dilute the solution to 100 ml with water (stock solution). Standardize the stock solution by titration with EDTA. Before use, dilute the stock solution to the appropriate concentration.

General procedure

Transfer an aliquot of the standard bismuth solution containing an appropriate amount of bismuth to a 100-ml or a 200-ml separatory funnel. Adjust the hydrobromic acid concentration to 0.05–0.1 *M* (final volume: 50 ml or 150 ml) and extract bismuth with 5 ml of a 5% (v/v) solution of tri-*n*-octylamine in benzene by shaking for 5 min. Discard the aqueous layer; wash the organic layer twice with 50-ml portions of 0.1 *M* hydrobromic acid, if necessary. Measure the absorbance of the organic layer at 380 nm against a reagent blank taken through the procedure.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows the absorption spectra of the complex of bismuth extracted with tri-*n*-octylamine in benzene, chloroform, and carbon tetrachloride solutions from 0.1 *M* hydrobromic acid solution. The absorption maxima of the extracts with tri-*n*-octylamine in benzene and in carbon tetrachloride were at 380 and 382 nm, respectively. The absorbance of the extract with tri-*n*-octylamine in chloroform was very low. In this study, tri-*n*-octylamine in benzene was adopted for the determination of bismuth. It can be seen from Fig. 1 that the absorbance of the reagent blank is very low at the wavelength of maximal absorption (380 nm) of the bismuth complex.

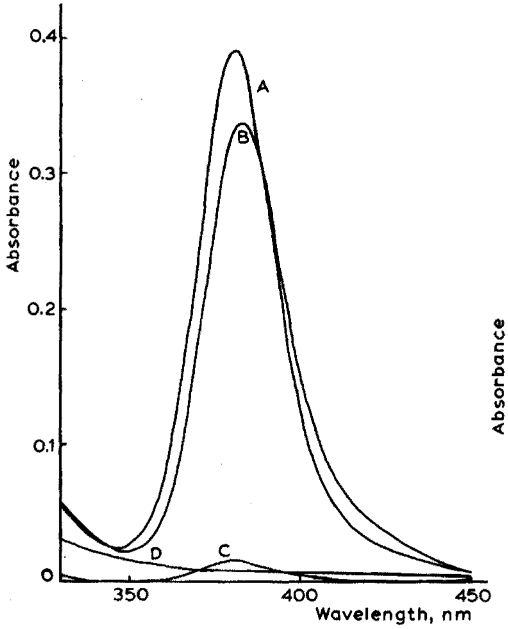
Effect of hydrobromic acid concentration

A series of solutions containing 20 μg of bismuth was prepared and the hydrobromic acid concentration of each solution was adjusted; the final volume of the aqueous phase was 50 ml. Bismuth was extracted with tri-*n*-octylamine in benzene and the absorbance of the extract at 380 nm was measured. The results (Fig. 2) show that bismuth could be best extracted from 0.05–0.2 *M* hydrobromic acid. The absorbance of the reagent blank was very low and increased gradually with an increase in the hydrobromic acid concentration.

Extraction with tri-n-octylamine

The effect of the concentration of tri-*n*-octylamine in benzene on the absorbance was investigated. Maximal absorbance was obtained with 3–10% (v/v) tri-*n*-octylamine in benzene. With less than 3% tri-*n*-octylamine, the percentage extraction decreased rapidly. A 5% solution of tri-*n*-octylamine in benzene was chosen.

An examination of the extraction of 20 μg of bismuth with one 5-ml or 10-ml portion of tri-*n*-octylamine in benzene, or with two 2.5-ml or 5-ml portions of



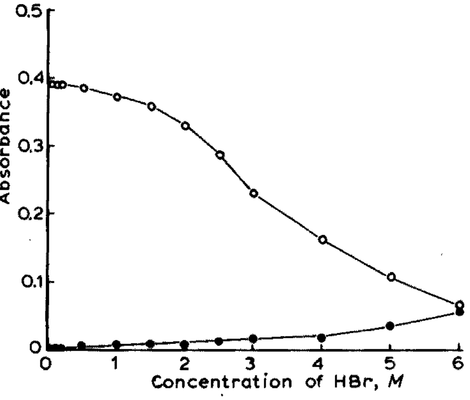


Fig. 1. Absorption spectra of a bromo-complex of bismuth extracted with tri-*n*-octylamine. Bi taken 40 μg; hydrobromic acid concentration 0.1 *M*. Solvent used: 10 ml of (A) 5% (v/v) tri-*n*-octylamine–benzene, (B) 5% (v/v) tri-*n*-octylamine–carbon tetrachloride, (C) 5% (v/v) tri-*n*-octylamine–chloroform, (D) 5% (v/v) tri-*n*-octylamine–benzene (reagent blank against the solvent). Absorbances measured against reagent blank for A, B, C.

Fig. 2. Effect of hydrobromic acid concentration. Solvent used 5% (v/v) tri-*n*-octylamine in benzene. (○) Bi taken 20 μg, absorbance against reagent blank; (●) absorbance of reagent blank against solvent.

the solvent from 0.1 *M* hydrobromic acid solution, showed that differences in the final absorbances were negligible. A single extraction with 5 ml of tri-*n*-octylamine in benzene was therefore chosen.

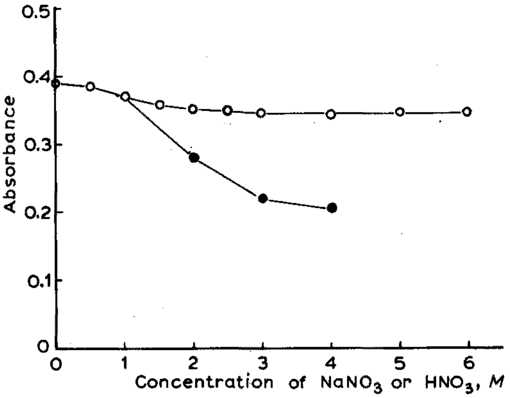
The shaking time for the extraction was varied from 1 to 10 min; the absorbance was found to be independent of the shaking time, and a period of 5 min was selected.

The color of the extract was found to be stable for at least 2 h.

Effects of diverse acids

As it was convenient to use nitric acid for the decomposition of the samples (lead, copper, nickel metals and copper-base alloys), the effect of nitrate ion was first investigated. It was found that the color development of bismuth in the tri-*n*-octylamine–benzene extract was depressed by sodium nitrate, but restored by washing the extract twice with 50-ml portions of 0.1 *M* hydrobromic acid; the effect of additional washings was negligible.

The effect of nitrate ion on the absorbance is illustrated in Fig. 3. The absorbance decreased gradually with an increase in the sodium nitrate concentration and reached a constant value above 3 *M* sodium nitrate. The depressive effect of nitric acid on the absorbance was much larger than that of sodium nitrate for



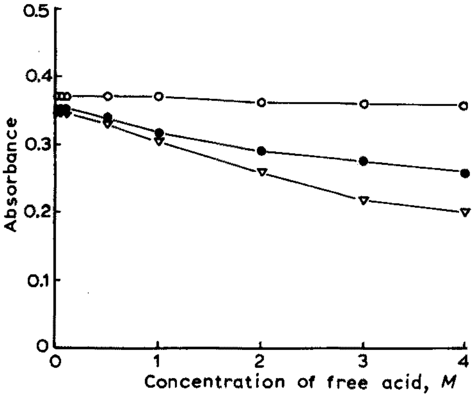


Fig. 3. Effects of sodium nitrate and nitric acid in the aqueous phase. Bi taken, 20 μg; hydrobromic acid concentration, 0.1 *M*; final volume of aqueous phase, 50 ml; solvent used, 5 ml of 5% (v/v) tri-*n*-octylamine in benzene; washing with 2 × 50 ml of 0.1 *M* hydrobromic acid. Addition: (○) $NaNO_3$, (●) HNO_3.

Fig. 4. Effect of free acid in the presence of nitrate ion. Conditions as for Fig. 3. Nitrate ion concentration (added as sodium nitrate): (○) 1 *M*; (●) 2 *M*; (▽) 3 *M*.

equal molarities. In Fig. 4, the effect of the free acid added as sulfuric acid (which had no effect on the absorbance) is shown; obviously, in the presence of nitrate ion, the free acid must be below 0.1 *M* (that is, $pH \geqq 1$).

As described above (Fig. 2), bismuth could best be extracted from up to 0.2 *M* hydrobromic acid. However, the presence of nitrate narrowed the optimal hydrobromic acid concentration range for the extraction to 0.05–0.1 *M* (Fig. 5).

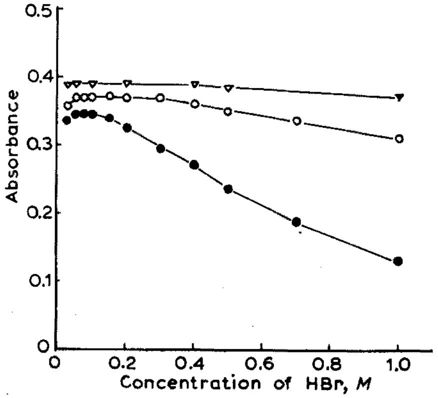
The effects of sulfuric, hydrochloric, perchloric and phosphoric acids on the absorbance were also investigated. Up to 5 *M* sulfuric acid and up to 1 *M* hydrochloric acid had no effect, but perchloric acid severely diminished the absorbance (Fig. 6). More than 0.01 *M* perchloric acid interfered. There was no interference from up to 1 *M* phosphoric acid.

Effects of various elements

As it was intended to determine bismuth in lead, copper and nickel metals, and in copper-base alloys, the effects of large amounts of lead, copper, nickel, and zinc on the determination of bismuth were first studied. The results (Table I) show that up to 5 g of copper, nickel or zinc did not interfere, but more than 0.1 g of lead interfered. This interference could be eliminated by washing the organic layer once with 50 ml of 0.1 *M* hydrobromic acid–2 *M* sodium nitrate solution (wash solution A) and then twice with 0.1 *M* hydrobromic acid. In the presence of more than 1 g of lead, 0.05 *M* hydrobromic acid concentration was preferable to 0.1 *M*, because lead bromide was precipitated when the hydrobromic acid concentration in the aqueous phase was 0.1 *M*.

The effect of shaking time for the washing was found to be negligible in the range of 1–10 min.

The interfering effects of other elements found generally in lead, copper, nickel metals, and copper-base alloys were then investigated. Amounts of 100 mg of Al^{3+}, Cr^{3+}, Fe^{3+}, Se(VI), Sn^{4+}, 10 mg of As(III), Cd^{2+}, Co^{2+}, In^{3+}, Mn^{2+}, Sb^{3+}, Te(VI), and 0.1 mg of Ag^{+} did not interfere.



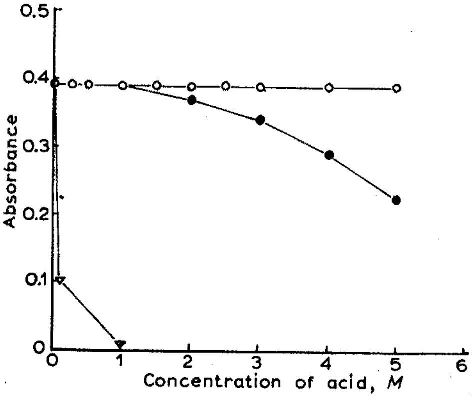


Fig. 5. Effect of hydrobromic acid concentration in the presence of nitrate ion. Conditions as for Fig. 3 except HBr concentration. Nitrate ion concentration (added as sodium nitrate): (▽) 0, (○) 1 *M*, (●) 3 *M*.

Fig. 6. Effects of diverse acids. Conditions as for Fig. 3. (○) H_2SO_4; (●) HCl; (▽) $HClO_4$.

TABLE I

EFFECTS OF LEAD, COPPER, NICKEL AND ZINC ON THE DETERMINATION OF BISMUTH

(Bi taken 20 μg; hydrobromic acid concentration 0.1 *M* except for Pb addition, in the case of Pb addition 0.05 *M*; nitrate concentration 2 *M* (elements were added as nitrate and the nitrate ion concentration was adjusted with sodium nitrate); final volume of aqueous phase 150 ml; washing with 2 × 50 ml of 0.1 *M* hydrobromic acid)

Addition (g)	*Absorbance*	*Addition (g)*	*Absorbance*
No addition	0.272	No addition	0.272
Zn 1	0.278	Pb 0.05	0.276
Zn 3	0.273	Pb 0.1	0.285
Zn 5	0.277	Pb 0.3	0.313
Ni 1	0.273	Pb 0.5	0.334
Ni 3	0.272	Pb 0.8	0.360
Ni 5	0.277	Pb 1	0.409
Cu 1	0.274	Pb 5	0.547
Cu 3	0.275	No addition	0.255[c]
Cu 5	0.272	Pb 1	0.258[c]
No addition	0.345[b]	Pb 3	0.255[c]
Cu 1[a]	0.347[b]	Pb 5	0.254[c]

[a] Added as sulfate.

[b] Nitrate ion concentration 0; sulfuric acid concentration 1 *M*; final volume of aqueous phase 50 ml; washing with 50 ml of wash solution A and with 2 × 50 ml of 0.1 *M* hydrobromic acid.

[c] Washing with wash solution A and then twice with 0.1 *M* hydrobromic acid.

DETERMINATION OF BISMUTH IN LEAD, COPPER, NICKEL METALS, AND COPPER-BASE ALLOYS

Recommended procedure

Determination of bismuth in copper and nickel metals, and in copper-base alloys. Dissolve 5 g of sample in 40 ml of nitric acid (1 + 1). Cool and adjust the pH to 2.0–2.2 with sodium hydroxide solution. Transfer with 15.0 ml of 1 *M* hydrobromic acid to a 200-ml separatory funnel and make up to 150 ml with water. Shake vigorously with 5.0 ml of 5% (v/v) tri-*n*-octylamine in benzene solution for 5 min. Discard the aqueous layer. Shake vigorously the organic layer with 50 ml of the wash solution A for 5 min. Discard the aqueous layer. Shake the organic layer vigorously with 50 ml of 0.1 *M* hydrobromic acid for 5 min. Discard the aqueous layer. Wash the organic layer with 50 ml of 0.1 *M* hydrobromic acid and discard the aqueous layer. Measure the absorbance of the organic layer at 380 nm against a reagent blank.

Prepare the calibration curve as follows. Transfer aliquots of the standard bismuth solution (0–50 μg Bi) to 200-ml separatory funnels. To each solution and a blank (water), add 60 ml of 5 *M* sodium nitrate solution and 15.0 ml of 1 *M* hydrobromic acid. Make the volume up to 150 ml with water. Continue as described above and measure the relationship between the absorbance and the amounts of bismuth.

Determination of bismuth in lead metal. Dissolve 5 g of sample in 20 ml of nitric acid (1 + 1). Cool and add 30 ml of 5 *M* sodium nitrate solution. Adjust the pH to 2.0–2.2 with sodium hydroxide solution. Transfer with 7.5 ml of 1 *M* hydrobromic acid to a 200-ml separatory funnel and make up to 150 ml with water. Determine the amount of bismuth as described above.

Prepare the calibration curve as follows. Transfer aliquots of the standard bismuth solution (0–50 μg) to 200-ml separatory funnels. To each solution and a blank (water), add 60 ml of 5 *M* sodium nitrate solution and 7.5 ml of 1 *M* hydrobromic acid. Make the volume up to 150 ml with water. Continue as described above.

Determination of bismuth in anode copper. Decompose 1 g of sample with 5 ml of nitric acid (1 + 1) and 5 ml of hydrochloric acid (1 + 1). Add 10 ml of sulfuric acid (1 + 1) and evaporate the solution to fumes. Add water to dissolve the solids precipitated. Transfer with 5.0 ml of 1 *M* hydrobromic acid to a 100-ml separatory funnel and make up to 50 ml with water. Determine the amount of bismuth as described above.

Prepare the calibration curve as follows. Transfer aliquots of the standard bismuth solution (0–50 μg) to 100-ml separatory funnels. To each solution and a blank (water), add 5.0 ml of 1 *M* hydrobromic acid. Make the volume up to 50 ml with water. Continue as described above.

Results

The results of the determination of bismuth in a variety of lead, copper and nickel metals, and of copper-base alloys are shown in Table II. The results were in good agreement with those found by other methods. The precision of the method was good, and the detection limit by this method was 1 μg of bismuth. The proposed method is rapid, sensitive, and considered to be satisfactory.

TABLE II

ANALYTICAL RESULTS FOR LEAD, COPPER, NICKEL METALS, AND COPPER-BASE ALLOYS

Sample	*Composition (%)*	*Bi determined (p.p.m.)*	
		Proposed method	*Other method*
Lead metal (sheet)	Pb > 99.9	4.4, 4.5, 4.5	5.4[b]
Lead metal (shot)	Pb > 99.9	6.4, 6.7, 6.9	7.5[b]
Copper metal (VMC)	Cu > 99.99	0.4, 0.5, 0.5	< 1[c]
Copper metal (tough pitch)	Cu > 99.90	1.2, 1.4, 1.5	1.4[c], 1.0[b]
Anode copper	Cu > 98.0[a]	22, 24, 25	27[b]
Nickel metal (electrolytic)	Ni > 99.9	< 0.4, < 0.4	< 0.4[b]
Brass	Cu: 70.34 Zn: balance	0.7, 0.7, 0.6	
Leaded brass	Cu: 59.63 Pb: 1.21 Fe: 0.02 Zn: balance	0.6, 0.6, 0.7	
Nickel silver	Cu: 55.11 Ni: 18.20 Mn: 0.27 Zn: balance	0.6, 0.6, 0.5	

[a] Several components other than copper: Ag 0.05, Sb 0.15, Ni 0.07, Fe 0.02, Se 0.01, Pb 0.08, As 0.18 and Sn 0.004%.

[b] Atomic absorption spectrometry[9].

[c] Emission spectrometry.

SUMMARY

A rapid and sensitive spectrophotometric method has been developed for the determination of bismuth in lead, copper and nickel metals, and in copper-base alloys. Optimal conditions have been established for the extraction and determination of bismuth. Bismuth is extracted with a benzene solution of tri-*n*-octylamine in the presence of hydrobromic acid and the absorbance of the extract (bromo-complex of bismuth) at 380 nm is measured. As little as 0.5 p.p.m. of bismuth in these metals and alloys can be determined.

RÉSUMÉ

Une méthode spectrophotométrique, rapide et sensible, est proposée pour le dosage du bismuth dans le plomb, le cuivre et le nickel, ainsi que dans les alliages à base de cuivre. Les conditions optimales ont été établies pour l'extraction et le dosage du bismuth. On procède à une extraction dans une solution benzènique de tri-*n*-octylamine, en présence d'acide bromhydrique. On effectue les mesures d'absorption à 380 nm. On peut ainsi doser des quantités minimales de bismuth allant jusqu'à 0.5 p.p.m. dans ces métaux et alliages.

ZUSAMMENFASSUNG

Für die Bestimmung von Wismut in Blei, Kupfer und Nickel sowie in Kupferlegierungen wurde eine schnelle und empfindliche spektrophotometrische Methode entwickelt. Die optimalen Bedingungen für die Extraktion und Bestimmung von Wismut wurden untersucht. Wismut wird mit einer benzolischen Lösung von Tri-*n*-octylamin in Gegenwart von Bromwasserstoffsäure extrahiert; die Extinktion des Extraktes (Bromokomplex von Wismut) wird bei 380 nm gemessen. 0.5 p.p.m. Wismut können in diesen Metallen und Legierungen bestimmt werden.

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QUANTITATIVE EXTRAKTIVE ABTRENNUNG VON ZIRKON UND TITAN MIT HILFE VON *n*-HEPTYLARSONSäURE

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Bei der Untersuchung der Extraktionswirkung aliphatischer Carbonsäuren zeigte sich, dass ab einer gewissen Kohlenstoff-Kettenlänge Metallextraktionen unter Verwendung von Chloroform als Lösungsmittel möglich sind, die in Umfang und Ausmass mit zunehmender Kohlenstoffanzahl steigen[1]. Caprinsäure[2] und Capronsäure[3] sind beispielsweise auch schon früher zu Metallextraktionen herangezogen worden.

Wenn man ins Auge fasst, dass die als Extraktionsmittel so weit verbreiteten Ketone verschiedenster Zusammensetzung mit den Carbonsäuren insoferne strukturell im Zusammenhang stehen, dass die Hydroxylgruppe der Carboxylgruppe durch einen aliphatischen Rest ersetzt ist, so lässt sich ein ähnliches Verhalten auch bei den Arsonsäuren erwarten. Arsinsäuren, die zwei Hydroxylgruppen der anorganischen Arsensäure durch aliphatische Reste ersetzt enthalten, haben eine ganz ausgezeichnete Extrahierbarkeit ihrer Metallverbindungen ergeben[4,5]. Dementsprechend liess sich auch bei aliphatischen Arsonsäuren eine Extrahierbarkeit von Metallverbindungen vermuten.

Die diesbezüglich angestellten Versuche bestätigten diese Vermutung und liessen im Falle der *n*-Heptylarsonsäure besonders für die Metalle Zirkon und Titan eine ausgezeichnete Extrahierbarkeit in Chloroform bei einer bemerkenswerten Acidität erkennen. Aus diesem Grunde wurde die extraktive Abtrennbarkeit dieser beiden Metalle in Form ihrer Verbindungen mit *n*-Heptylarsonsäure unter Verwendung von Chloroform als Extraktionsmittel bearbeitet.

Zur Ermittlung des besten Aciditätsgebietes für die Extraktion wurden 36.4 mg Zirkon, bzw. 19.1 mg Titan in 80 ml wässriger Phase verschiedener Acidität mit einer Lösung von 448 mg Heptylarsonsäure in 20 ml Chloroform einmal ausgeschüttelt. Dabei ergab sich für Zirkon, dass das Ausmass der Extraktion um den pH 6 sprunghaft ansteigt und im Gebiet von 0.1–1.0 *M* Salzsäure das Maximum hat. Gegen noch stärkere Aciditäten sinkt das Extraktionsausmass wieder ab. Für Titan ergab sich fast das gleiche Verhalten, nur ist in diesem Falle die Extraktionsausbeute bis zu einer Normalität von 6 *M* nicht wesentlich vermindert. Bei diesen rohen Vorversuchen wurde bereits eine fast 100%-ige Extraktion erreicht. Es sei auch ausdrücklich betont, dass an Stelle der verwendeten Salzsäure auch Salpeter- oder Schwefelsäure verwendet werden kann.

BESTIMMUNG DER METALLE IN DEN EXTRAKTEN

Ein Problem stellte die Bestimmung der Metalle in den Extrakten dar.

Dazu wurde sowohl die gravimetrische, die titrimetrische wie auch die, namentlich für Mikrobestimmungen wichtige, spektralphotometrische Bestimmungsmethode in Betracht gezogen.

Zur gravimetrischen Bestimmung von extrahiertem Zirkon wurde durch Vorversuche festgehalten, dass Zirkon auch in Gegenwart von Heptylarsonsäure, gebunden oder in freier Form, sowie in Gegenwart von Chloroform, anstandslos zu Zirkondioxyd verglüht werden kann. Dabei wurde sowohl die Variante geprüft, nach der das Chloroformextrakt nach Überschichten mit angesäuertem Wasser verkocht wurde und das Metall anschliessend zur Fällung kam, wie auch die Möglichkeit, das Extrakt direkt in einem konstant gewogenen Porzellantiegel unter einer Rotlichtlampe einzudampfen und den Rückstand anschliessend ebenfalls zu Zirkondioxyd zu verglühen. Die entsprechenden Versuche mit Titan verliefen analog, mit Titandioxyd als Glührückstand.

Die Möglichkeit einer Titration des Zirkons in den Extrakten mit Äthylendiammintetraessigsäure wäre schon aus arbeitstechnischen Gründen äusserst wünschenswert. Auf Titan treffen diese Überlegungen naturgemäss nicht zu. Die direkte Titration von Zirkon in Gegenwart von Heptylarsonsäure ist nicht möglich. Auch die Rücktitration mit Hilfe von Thoriumnitratlösung ist gestört. Es ist auch nicht möglich das Zirkon aus dem Chloroformextrakt durch Säurelösungen oder andere komplexbildende Agentien zurückzuextrahieren, da einerseits die anwendungsfähigen Säuren nicht stark genug sind die Zirkon–Heptylarsonsäureverbindung zu zerstören, andererseits Komplexbildungsmittel wie Oxalsäure die Titration ihrerseits erheblich stören. Es bleibt somit, wenn eine Titration unbedingt durchgeführt werden soll, nur die Möglichkeit nach Vertreiben des Chloroforms den Rückstand normal aufzuschliessen und die dabei gebildete Arsensäure durch Reduktion und Abtreiben als Arsentrichlorid zu verflüchtigen, da auch Arsensäure die chelatometrische Titration stört. Dazu wurde mehrere male mit einer Lösung von Hydrazinsulfat und Kaliumbromid in Salzsäure abgeraucht. Erst dann kann man die normale Titration vornehmen. Wenn man jedoch den ganzen dazu notwendigen Arbeitsaufwand in Betracht zieht, wird der Vorteil der Titrationsmethode gegenüber der gravimetrischen Arbeitsweise fragwürdig.

Die Möglichkeit der spektralphotometrischen Bestimmung hat besonders für Extraktionen im Mikrobereich Bedeutung. Um Zirkon solcherart zu erfassen stehen nach der Literatur eine Reihe von Methoden zu Verfügung. Von diesen wurde willkürlich die Methode von Flaschka und Farah[6] herausgenommen und auf die hier vorliegenden Verhältnisse angepasst. Diese Methode verwendet die mit Brenzkatechinviolett und Zirkon entstehende Färbung um geringe Mengen von Zirkon zu bestimmen. Bei Versuchen die in Anwesenheit von Heptylarsonsäure durchgeführt wurden stellte sich heraus, dass dann überhaupt keine Reaktion zwischen Brenzkatechinviolett und Zirkon eintrat. Somit war es im Mikrobereich ebenfalls notwendig aufzuschliessen. Da Versuche auch ergaben, dass Arsensäure eine gewisse Beeinflussung der Farbintensität der Zirkonverbindung zur Folge hat, wurde bei sämtlichen Mikroversuchen der Extraktrückstand aufgeschlossen und das Arsen durch Abrauchen vertrieben. Da es sich bei Mikroarbeiten nur um ganz geringe Mengen handelt, ist der dazu nötige Zeitaufwand minimal und im Hinblick auf die Gesamtbestimmung vertretbar. Nach der angegebenen Originalvorschrift wurde eine Eichkurve aufgestellt die im Bereiche von 1.0 μg bis 5.0 μg linear ist. Hydrazin und

Bromid im Überschuss beeinflussen die Ergebnisse nicht.

Auch für die Mikrobestimmung des Titans standen mehrere Methoden zur Verfügung. Wir wählten die schon lange bekannte und einfache Bestimmung mit Hilfe von Wasserstoffperoxyd nach der Angabe von Bendig und Hirschmüller[7]. Bei der Untersuchung des Einflusses von Heptylarsonsäure und Arsensäure auf die Titanfärbung zeigte sich, dass die Arsonsäure zwar die Färbung nicht verhindert, aber in ihrer Intensität verändert. Arsensäure hingegen beeinflusst die Farbbildung auch in 1000-fachen Überschuss gegenüber dem Titan überhaupt nicht. So konnte im Falle des Titans die photometrische Bestimmung unmittelbar im Anschluss an den Aufschluss ohne Abrauchen des Arsens erfolgen. Die verwendete Eichkurve konnte von reinen Titansalzlösungen übernommen werden da es sich herausstellte, dass eine vorher ausgeführte Extraktion mit Aufschluss keinerlei Einfluss auf die erhaltenen Werte ausübte.

EXTRAKTIONSDURCHFÜHRUNG

Schon bei der Bestimmung des optimalen pH-Gebietes für die Extraktion wurde ein 5-facher molarer Reagensüberschuss verwendet. Um den für eine gute Extraktion notwendigen Überschuss festzulegen wurden unter sonst gleichen Arbeitsbedingungen die jeweils zur Extraktion von Zirkon und Titan angewendeten Heptylarsonsäuremengen variiert. Es zeigte sich bei Zirkon, dass, abgesehen von einer Niederschlagsbildung in der wässrigen Phase, bis zu einem 3-fachen molaren Reagensüberschuss gegenüber dem Metall praktisch keine Zirkonextraktion stattfindet. Die Lösungen sind ausserdem trüb und lassen sich schlecht trennen. Wenn der Reagensüberschuss vierfach ist, werden die wässrige und organische Phase schlagartig klar, es erfolgt gute Schichttrennung und die Extraktion erreicht 100% der eingesetzten Zirkonmenge. Ein grösserer Überschuss ist durchaus möglich und unschädlich, hat jedoch auch keine verbessernden Wirkungen mehr.

Bei Titan bietet sich ein etwas abweichendes Bild. Bei einem bis zu zweifachem Reagensüberschuss besteht schlechte Phasentrennung, Schaumbildung und minimale Extraktion. Ab einem 2.5-fachen Reagensüberschuss über das Titan wird die Trennung der trüb bleibenden Phasen gut, die Extraktion steigt auf über 90%. Aber auch hier wird eine quantitative Extraktion erst bei einem vierfachen molaren Überschuss an Reagens erreicht, begleitet von klaren Phasen und guter Trennung.

Man kann daraus ersehen, dass sowohl beim Zirkon wie auch beim Titan ein mindestens vierfacher molarer Überschuss an Reagens vorhanden sein muss, wenn man eine quantitative Extraktion erzielen will. Dabei sei aber darauf hingewiesen, dass es sich bei den bisher angegebenen Extraktionen um Einzelextraktionen handelte, die damit erreichbare 100%ige Extraktion also durchaus bemerkenswert ist und einen Hinweis auf die Stabilität der extrahierten Verbindungen gibt.

Allgemeine Arbeitsvorschrift

Die Metallsalzlösung wird in einem Schütteltrichter mit 0.5 M Salzsäure, oder gegebenenfalls auch Salpeter- oder Schwefelsäure, auf ein Volumen von 80 ml verdünnt. Hierauf setzt man 20 ml Chloroform, die 900 mg *n*-Heptylarsonsäure in diesem Volumen enthält, zu und schüttelt nach Verschliessen kräftig durch. Hierauf wird der Glasstopfen zum Druckausgleich vorsichtig gelüftet, zum Schluss unter

Abspülen mit reinem Chloroform entfernt. Sollte es zu einer Schaumbildung gekommen sein, was einen zu geringen Reagenszusatz anzeigt, so werden zusätzlich noch weitere Anteile der obigen Reagenslösung zugesetzt, bis nach neuerlichem Schütteln gute Schichtentrennung eintritt.

Danach wird die das Zirkon bzw. Titan und die Säure enthaltende Chloroformphase in ein Sammelgefäss abgelassen, und das Hahnküken von aussen mit reinem Chloroform sorgfältig abgespült.

Zur Sicherheit wird der im Schütteltrichter verbliebenen wässrigen Schicht nochmals etwa 5 ml der Reagenslösung zugesetzt und nachextrahiert, wobei das Chloroformextrakt mit der Hauptmenge vereinigt wird. Anschliessend wird noch zweimal mit je 5 ml reinem Chloroform nachgeschüttelt und auch dieses zu den Chloroformextrakten gegeben.

Die vereinigten Chloroformextrakte werden nun nach einer der bereits besprochenen Methoden nach Entfernen des Chloroforms auf die enthaltenen Metalle aufgearbeitet.

Die Tabelle I zeigt nach dieser Arbeitsmethode erhaltene Werte von Testlösungen der Reinmetalle in Makro- und Mikromengen.

TABELLE I

TESTEXTRAKTIONEN AUS REINLÖSUNGEN

Makromengen			*Mikromengen*		
Gegeben (mg)	*Gefunden (mg)*	*% F*	*Gegeben (μg)*	*Gefunden (μg)*	*%F*
Zirkon			*Zirkon*		
9.73	9.72	−0.1	136	140	+2.4
38.9	39.0	+0.2	182	183	+0.5
77.8	78.0	+0.2	227	228	+0.5
97.3	97.2	−0.1			
Titan			*Titan*		
8.64	8.64	±0.0	140	140	±0.0
34.6	34.5	−0.2	200	200	±0.0
69.1	69.1	±0.0	600	600	±0.0
86.4	86.4	±0.0	1800	1800	±0.0

TRENNUNGEN

Die angegebene allgemeine Arbeitsvorschrift für Einzelbestimmungen sieht eine Acidität von 0.5 M an Salz,- Salpeter- oder 0.25 M an Schwefelsäure vor. Bei dieser hohen Acidität verbinden sich nur relativ wenige andere Metalle mit der *n*-Heptylarsonsäure und sind daher auch nur wenige Metalle extrahierbar. Daher wurde die angegebene allgemeine Arbeitsvorschrift auch unverändert für Trennungen herangezogen, wobei teilweise auch die abgetrennten Metallionen in den nach der Chloroformextraktion verbleibenden wässrigen Schichten bestimmt wurden. Bei höheren Mengen an Begleitmetallen wurden auf deren Bestimmung verzichtet, da die Tatsache dass sie nicht mitextrahiert wurden auch aus den gefundenen Zirkon- bzw. Titanwerten ersichtlicht ist.

TABELLE II

ABTRENNUNG DES ZIRKON VON BEGLEITMETALLEN

(58.4 mg Zirkon gegeben)

Gefunden Zirkon (mg)	*Begleitmetall (mg)*			*Gefunden Zirkon (mg)*	*Begleitmetall (mg)*		
	Metall	*Gegeben*	*Gefunden*		*Metall*	*Gegeben*	*Gefunden*
58.4	NH_4	1700	—	58.4	Co	600	—
58.5	Na	1960	—	58.3	Zn	52.0	52.0
58.6	K	2620	—	58.5	Zn	600	—
58.6	Mg	50.5	50.6	58.3	As(III)	200	—
58.6	Ca	53.0	53.0	58.5	Cu	52.2	52.2
58.5	Ca	600	—	58.7	Cu	600	—
58.4	Ba	51.2	50.9	58.3	Cd	51.2	51.2
58.5	Ba	600	—	58.3	Cd	600	—
58.5	Be	535.0	—	58.5	Pt(IV)	52.0	—
58.3	Al	600	—	58.4	Pd(II)	53.0	—
58.7	Cr(III)	57.2	57.3	58.4	Ce(III)	366.0	—
58.6	Mn	53.5	53.5	58.8	Ce(IV)	14.0	—
58.3	Mn	600	—	58.5	La	55.2	—
58.3	Ni	48.7	48.7	58.3	Si(IV)	28.0	—
58.5	Ni	600	—	58.4	Pb	50.5	50.7
58.5	Co	52.8	52.7	58.1	Pb	600	—

Die Tabelle II zeigt Beispiele solcher Trennungen bei Zirkon.

Zusammenfassend lässt sich über die Abtrennbarkeit des Zirkons von begleitenden Metallen sagen, dass dies ohne Schwierigkeiten auch bei grossem Überschuss der Begleitmetallionen von NH_4^+, Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Be^{2+}, Al^{3+}, Pb^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, As^{3+}, Cu^{2+}, Cd^{2+}, Pt^{4+}, Pd^{2+}, Ce^{3+} und La^{3+} möglich ist. Eisen in dreiwertiger Form sowie Vanadin können vor der Zirkonextraktion mit Aluminiummetall reduziert werden und sind dann ebenfalls abtrennbar. Keine Trennung ist wegen Schaum- und Niederschlagsbildung sowie Unmöglichkeit der Phasentrennung von den Ionen Fe^{3+}, V^{5+}, Sn^{2+}, Au^{3+}, W^{6+}, Hf^{4+}, Th^{4+} und Bi^{3+} möglich.

Erwähnt sei noch, dass die Anionen Chlorid, Sulfat, Nitrat, Acetat und Borat in beliebiger Menge vorhanden sein können, ohne die Extraktion zu stören. Weinsäure verhindert die Phasentrennung und Phosphation wird mitextrahiert.

Die Tabelle III bringt Beispiele der Abtrennung von Titan.

Zusammenfassend lässt sich über die Abtrennbarkeit von Titan sagen, dass diese bis zu einem hohen Verhältnis von den Begleitionen NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Be^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, As^{3+}, As^{5+}, Cu^{2+}, Cd^{2+} und Ce^{3+} möglich ist. Die Kationen Fe^{3+}, Ce^{4+}, Th^{4+} und UO_2^{2+} werden teilweise mitextrahiert. Eine vorherige Reduktion des Fe^{3+} durch Aluminiummetall ist jedoch auch hier möglich.

TABELLE III

ABTRENNUNG DES TITAN VON BEGLEITMETALLEN

(43.2 mg Titan gegeben)

Gefunden Titan (mg)	*Begleitmetall (mg)*		
	Metall	*Gegeben*	*Gefunden*
43.2	NH_4	1367	—
43.2	Na	1960	—
43.2	K	2620	—
43.2	Mg	50.5	50.5
43.2	Mg	600	—
43.2	Ca	53.0	53.0
43.2	Ca	600	—
43.2	Be	535.0	—
43.2	Al	25.9	25.9
43.2	Al	600	—
43.2	Fe(II)	505.0	—
43.2	Cr(III)	57.2	—
43.2	Mn	53.4	53.5
43.3	Mn	600	—
43.2	Ni	48.7	48.6
43.3	Ni	600	–
43.2	Co	52.8	52.7
43.3	Co	600	—
43.2	Zn	52.0	52.0
43.3	Zn	600	—
43.2	As(V)	6.1	—
43.3	As(III)	214.0	—
43.3	Cu	52.2	52.3
43.2	Cu	600	—
43.2	Cd	51.2	51.2
43.3	Cd	600	—
43.2	Ce(III)	366.0	—

TABELLE IV

TESTANALYSEN

Produkt	*Begleitbestandteile*	*Testbestimmung*	*Extraktionsmethode*
Ferrozirkonsilizium	Si, Fe, C	14.4% Zr	14.2% Zr
Stahl	Mn, Si, P, S, Cr, Al, C	0.31% Zr	0.28% Zr
Legierung	Al, Fe, Si, Cu, Mn, Mg	0.24% Ti	0.25% Ti
Glas	Si, B, Na, As	20.3% Ti	20.3% Ti

Die Anionen Sulfat, Chlorid, Nitrat, Acetat und Borat stören auch in grösseren Mengen nicht. Weinsäure, Phosphorsäure und Kieselsäure stören, wenn sie in grösseren Mengen anwesend sind.

Die guten Trennungsmöglichkeit die für Zirkon und Titan mit Hilfe von *n*-Heptylarsonsäure durch eine einfache Extraktion gegeben ist, wurde abschliessend noch an einigen technischen Produkten getestet.

In der Tabelle IV sind die Art der technischen Produkte, sowie die ausser den bestimmten Metallen vorhandenen Bestandteile nebst den Vergleichswerten angegeben.

Die Untersuchung weiterer Trennungsmöglichkeiten mit *n*-Heptylarsonsäure sowie der Zusammensetzung der betreffenden Verbindungen ist in Arbeit.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass sich Zirkon und Titan aus einer etwa 0.5 *N* sauren Lösung von Salz-, Salpeter- und Schwefelsäure mit *n*-Heptylarsonsäure rasch und einfach extrahieren lassen. Die Bestimmung der Metalle im Extrakt ist gravimetrisch, und nach gewissen Vorbereitungen auch massanalytisch und photometrisch möglich. Die Extraktion erlaubt gleichzeitig auch eine Abtrennung von einer Vielzahl von Elementen. Beleganalysen werden angegeben und Vergleichsanalysen technischer Produkte beigebracht.

SUMMARY

Zirconium and titanium can be easily and quickly extracted from *ca.* 0.5 *M* hydrochloric, nitric or sulphuric acid by means of *n*-heptylarsonic acid in chloroform. The metal can be determined gravimetrically, or after some pretreatment, titrimetrically or photometrically. The extraction allows a quantitative separation from a large number of elements. The results obtained for technical products such as alloys and glass are compared with results of standard methods.

RÉSUMÉ

On propose une séparation quantitative dú zirconium et du titane, par extraction, en utilisant l'acide *n*-heptylarsonique, dans le chloroforme. Le métal peut ensuite être dosé par gravimétrie ou, après un prétraitement, par titrimétrie ou photométrie. L'extraction permet une séparation quantitative d'avec un grand nombre d'éléments. Les résultats obtenus pour des produits techniques, tels que alliages et verre sont comparés avec ceux de méthodes classiques.

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ATOMIC EMISSION SPECTROMETRY WITH AN INDUCTION-COUPLED HIGH-FREQUENCY PLASMA SOURCE

THE DETERMINATION OF IODINE, MERCURY, ARSENIC AND SELENIUM

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The application of an inductively coupled high-frequency plasma source to the determination of sulphur and phosphorus in aqueous solution at their resonance lines at wavelengths less than 200 nm has been described recently[1]. The present paper reports the application of this source to the determination of arsenic, iodine, mercury and selenium in aqueous solution; the resonance lines of these elements also lie below 200 nm.

The direct emission spectrometric determination of iodine with microwave (2450 MHz)[2] and r.f. (3 MHz)[3] plasmas at the iodine non-resonance line has been reported. Iodine has also been determined directly at 183.04 nm by atomic absorption spectrometry in a graphite cuvette[4] and in a nitrogen-separated nitrous oxide–acetylene flame[5]. In the emission methods described to date, the detection limits are relatively poor because of the relatively low energy excitation conditions and the use of the non-resonance lines. The plasma used in the present study is of considerably higher power than those used by other workers for the excitation of the iodine atomic spectrum, and the modifications to the detection system allow observation of the iodine ground-state lines at 178.28 nm and 183.04 nm.

The determination of traces of mercury is obviously of considerable importance in environmental pollution studies. The spectrometric methods most frequently used for the determination of such quantities of mercury employ a cold vapour technique in which the mercury is measured by atomic absorption spectrometry at 253.65 nm. The conventional flame absorption and fluorescence techniques also use the mercury 253.65-nm line; it may be calculated, however, that the use of the mercury 184.96-nm line should provide a considerable gain in signal strength over that obtained at the 253.65-nm line although its application does require modification of the detection system. As the determination of mercury in a high-power r.f. plasma source spectrometer would be expected to yield high sensitivity, utilization of the ground-state 184.96-nm line should enable nanogram quantities of mercury to be detected.

The determination of arsenic at the sub-part per million level is of particular importance to the food industry because of the legislation regarding the use of this element. Both arsenic and selenium have been determined by atomic absorption spectrometry in argon–hydrogen[6,7], air–acetylene[8–11], and separated nitrous oxide–acetylene[12] flames. The detection limits reported in these flames are *ca.* 0.7 p.p.m. and 0.6 p.p.m. for arsenic and selenium, respectively, when the arsenic 193.69-nm and selenium 196.03-nm lines are used. Extensive chemical interferences are observed from common ions when cool flames are used. The use of the separated nitrous oxide–acetylene flame overcomes these interference effects; although no loss in detection limit is incurred, the sensitivity (for 1% absorption) is poorer.

Dickinson and Fassel have reported the determination of arsenic at 228.81 nm with an r.f. plasma source[13]. These workers obtained a detection limit of 0.1 p.p.m. with their system which employed an ultrasonic nebulizer and desolvation before the solute entered the plasma. No interference study was reported, but it seems possible that some spectral interference would occur from cadmium, cobalt and nickel.

In the apparatus used in this study, only a simple indirect nebulizer and expansion chamber are used to introduce aqueous sample solutions into the plasma. The object of the work was to obtain high sensitivity for arsenic and selenium by means of their ground-state atomic lines at wavelengths less than 200 nm.

EXPERIMENTAL

Apparatus

The modifications made to a Techtron AA4 atomic absorption spectrophotometer to permit detection of radiation at wavelengths below 200 nm from the tailflame of the Radyne Model H30/P plasma generator have been detailed previously[1]. The most important modification is the provision of a method for purging the monochromator and optical path between the plasma and entrance slit with nitrogen.

Reagents

All reagents used were of analytical-reagent grade.

A stock 10,000-p.p.m. iodine solution was prepared by dissolving ammonium iodide in distilled water.

Stock 1000-p.p.m. solutions of mercury(I) and mercury(II) were prepared by dissolving the respective nitrates in *ca.* 10 ml of concentrated nitric acid and dilution to volume with distilled water.

A 1000-p.p.m. arsenic stock solution was prepared by dissolving arsenic trioxide in 2 *M* hydrochloric acid. A second stock solution, made primarily to investigate the effect of excess chloride, was prepared by dissolving arsenic trioxide in sodium hydroxide solution and then diluting the volume with distilled water.

A 1000-p.p.m. stock solution of selenium was prepared by dissolving sodium selenite in distilled water.

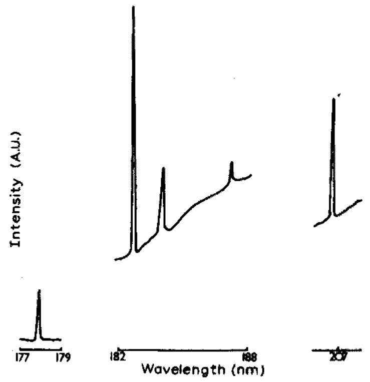
RESULTS

Spectral characteristics

Figure 1 shows a wavelength scan of the iodine atomic-emission spectrum obtained over the range 177–208 nm when 600 p.p.m. of iodine was introduced into the plasma as aqueous ammonium iodide. The 206.16-nm line is not reduced in intensity by absorption by air or quartz as are the resonance lines at 183.04 and

178.28 nm. The photomultiplier response is also better at the 206.16-nm line than at the other two lines. Thus, of the three lines, the 206.16-nm non-resonance line gives the largest signal, although its signal-to-background ratio is the poorest.

The emission spectra obtained over the ranges 184–186 nm and 252–255 nm when 20 p.p.m. of mercury is introduced into the plasma as aqueous mercury(I) nitrate or mercury(II) nitrate are shown in Fig. 2. Although the emission intensity recorded at 253.65 nm is greater than that at 184.96 nm, for the same reasons as given above for iodine, the signal-to-background and signal-to-noise ratios are very much poorer at the former line. An enhanced signal is observed for mercury(I) compared to mercury(II). The same enhancement is observed at both lines, which indicates that the effect observed in a flame[14] also occurs in the plasma.



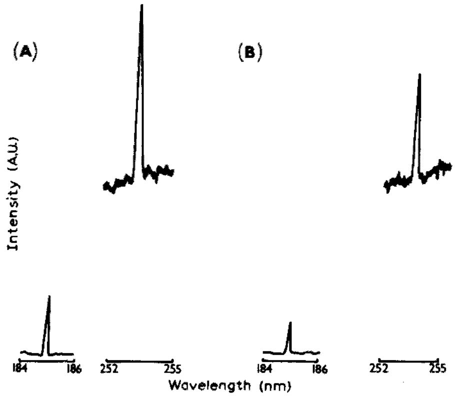


Fig. 1. Emission spectra in the ranges 177–179, 182–188 and 205–208 nm obtained for 600 p.p.m. of iodine introduced as aqueous ammonium iodide solution. Region 205–208 nm shown at $\frac{1}{4}$-intensity scale compared to 177–179 and 182–188 nm range.

Fig. 2. Emission spectrum obtained for 20 p.p.m. of mercury introduced as an aqueous solution of (A) mercury(I) nitrate; and (B) mercury(II) nitrate.

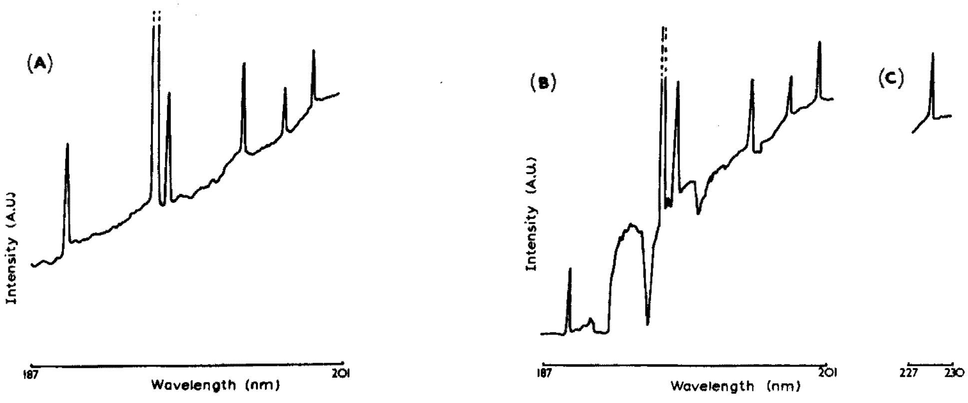


Fig. 3. Emission spectra obtained for 20 p.p.m. of arsenic introduced as an aqueous sodium arsenite solution. (A) Over the wavelength range 187–201 nm with purged optical path; (B) over the wavelength range 187–201 nm with unpurged optical path; and (C) over the wavelength range 227–230 nm.

Figure 3(A, B) shows the spectra obtained over the range 187–201 nm with and without purging of the optical path when 20 p.p.m. of arsenic was introduced as an aqueous sodium arsenite solution. Clearly, there is a great improvement in the signal-to-noise ratio at 189.0 nm when the monochromator is purged with nitrogen; the improvement is less marked at 193.69 nm. The spectrum obtained with an unpurged optical path shows the effect of air absorption on the background radiation; this effect is eliminated by nitrogen purging. The arsenic 228-nm line was also obtained (Fig. 3C) but with relatively poor signal-to-background ratio.

The emission spectra obtained in the range 194–198 nm for a 20-p.p.m. selenium solution, as aqueous sodium selenite, with and without purging of the optical path are shown in Fig. 4. Figure 4(C) shows the selenium emission spectrum obtained at 203–207 nm for a solution containing 40 p.p.m. of selenium.

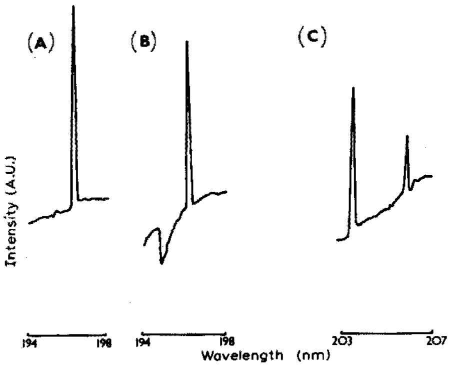


Fig. 4. Emission spectra obtained for 20 p.p.m. of selenium introduced as an aqueous sodium selenite solution. (A) Over the wavelength range 194–198 nm with purged optical path. (B) Over the wavelength range 194–198 nm with unpurged optical path. (C) Emission spectrum obtained at 203–207 nm from 40 p.p.m. of selenium introduced as aqueous sodium selenite solution.

Optimization of operating conditions

The elements investigated are relatively easily atomized but difficult to ionize, and their resonance lines have high excitation energies. These similarities result in similar optimal conditions for the height of observation of their atomic line spectra in the plasma tailflame[13]. The same observation height as used in earlier work[1], *i.e.* 16 mm above the top of the outer quartz tube was again employed.

Argon was used as both the injector and coolant gas; the injector flow-rate employed was 3 l min^{-1} and the coolant flow-rate was 15 l min^{-1}. The optimal sample uptake rate was found to be 4 ml min^{-1}. The power supplied to the work coil was optimized to produce best signal-to-noise ratios in the emission observed for each element and corresponds to a grid current of 0.41 A and a high-tension current of 1.0 A.

The spectral band pass employed was chosen to be as narrow as possible, to minimize spectral interferences, while still permitting sufficient radiant energy to reach the photomultiplier without operating the amplifier system at maximum gain. A slitwidth of 25 μm, corresponding to a spectral half-band pass of 0.08 nm, was chosen.

Detection, sensitivity and calibration graphs

Table I shows the relative emission intensities for the principal atomic lines observed for iodine, mercury, arsenic and selenium introduced into the plasma in aqueous solution. The corresponding detection limits obtained with the optimal operating conditions at these lines are also shown in Table I. The detection limits are defined as that concentration of analyte in aqueous solution which produces a signal equal to twice the standard deviation obtained in the background noise observed for solutions of concentration near the detection limit.

TABLE I

EMISSION CHARACTERISTICS FOR ELEMENTS INTRODUCED INTO PLASMA

Element		*Wavelength (nm)*	*Relative emission intensity (arbitrary units)*	*Detection limit (p.p.m.)*
Iodine		178.28	12	1.0
		183.04	50	0.8
		184.44	16	2.5
		187.64	3	15
		206.16	100	0.5
Mercury				
	Hg(I)	184.96	36	0.001
		253.65	100	0.030
	Hg(II)	184.96	22	0.002
		253.65	61	0.050
Arsenic		189.0	46	0.11
		193.69	50	0.10
		197.20	36	0.16
		198.97	15	0.30
		200.33	24	0.25
		228.81	100	0.13
Selenium		196.09	100	0.11
		203.44	72	0.16
		206.28	28	0.37

Calibration graphs were established for iodine, as ammonium iodide in aqueous solution, at the iodine 178.28-, 183.04- and 206.16-nm lines. Significant deviation from linearity in these graphs was observed above 6,000 p.p.m. for both the 178.28- and 183.04-nm resonance lines. The calibration graph for the 206.16-nm line, which is not a ground-state line and is therefore less affected by self-absorption at high concentration, is linear as far as 10,000 p.p.m. of iodine. This line is also the most intense observed for iodine, gives the lowest detection limit and does not require the use of nitrogen purging of the optical path.

Calibration graphs for both mercury(I) and mercury(II) were found to be linear to concentrations as high as 700 p.p.m. in aqueous solution at both the 253.65- and 184.96-nm lines. The 184.96-nm line yielded a detection limit thirty times lower than that observed at the 253.65-nm line. The latter line is detected with greater intensity, but significantly better signal-to-noise is obtained at 184.96 nm.

The calibration graphs established for arsenic at the 189.0-, 193.69-, 197.20- and 228.81-nm lines were each found to be linear up to 50 p.p.m. of arsenic in aqueous solution. The 193.69-nm line provides the best attainable detection limit; nitrogen purging of the optical path results in only a small improvement in the detection limit although the signal intensity was enhanced significantly.

The selenium calibration graph established at 196.09 nm was linear to a concentration of 50 p.p.m. of selenium in aqueous solution.

Effect of foreign ions

The effect of a range of other cations and anions on the determination of iodine, mercury, arsenic and selenium was investigated separately for each element. An ion was considered to interfere when it produced an error in the emission intensity of greater than twice the standard deviation in the measurement of the analyte alone.

TABLE II

EFFECT OF INTERFERING IONS ON EMISSION INTENSITIES

Analyte	*Foreign ion*	*Wavelength (in italics)(nm) and interference effect (%)*			
Iodine[a]		*178.28*	*183.03*	*206.16*	
	Co^{2+}	N.I.[b]	N.I.	+500	
	Cr^{3+}	+60	+70	+ > 1000	
	Cu^{2+}	+50	+45	+270	
	Fe^{3+}	+80	+80	+75	
	Mo^{6+}	N.I.	N.I.	+200	
	Ni^{2+}	N.I.	N.I.	+75	
	Zn^{2+}	N.I.	N.I.	+ > 1000	
	PO$_4^{3-}$	+240	N.I.	N.I.	
Mercury[c]		*184.96*		*253.65*	
		Hg(I)	Hg(II)	Hg(I)	Hg(II)
	Co^{2+}	N.I.	N.I.	+30	+60
	Fe^{3+}	N.I.	N.I.	+80	+130
	Mn^{2+}	N.I.	N.I.	+10	+20
	Mo^{6+}	N.I.	N.I.	+10	+15
	Ni^{2+}	N.I.	N.I.	+40	+70
	Sn^{2+}	N.I.	+80	N.I.	+70
	Cl^{-}	−80	N.I.	−80	N.I.
	PO$_4^{3-}$	N.I.	N.I.	+25	+40
Arsenic[c]		*189.0*	*193.69*	*288.81*	
	Co^{2+}	N.I.	N.I.	+65	
	Ni^{2+}	N.I.	N.I.	+100	
	Zn^{2+}	N.I.	+20	N.I.	

[a] 5,000 p.p.m. of foreign ion added; 100 p.p.m. of iodine used.

[b] N.I. = no interference.

[c] 500 p.p.m. of foreign ion added; 10 p.p.m. of mercury or arsenic used.

Iodine. The presence of a fifty-fold (weight) amount of the following ions did not affect the emission intensity obtained for 100 p.p.m. iodine as ammonium iodide: Al, Ca, K, Mg, Mn(II), Na, NH_4, acetate, chloride, fluoride, nitrate and sulphate. Those ions which exhibited interference at this level are shown in Table II. With the exception of the enhancement effects observed for Cr(III), Cu(II) and Fe(III), the interferences can be attributed to spectral emission from the foreign species present. On introduction of an aqueous chromium(III) chloride solution into the plasma, emission was observed at 178.28 and 183.04 nm; this may be attributed to the presence of iodide impurity in the chromium salt used. This was confirmed by the observation of atomic absorption at the iodine 183.04-nm line when the stock solution was nebulized into a nitrogen-shielded nitrous oxide–acetylene flame using a Perkin-Elmer Model 290B spectrometer fitted with an iodine electrodeless discharge lamp. The introduction of chromium into the plasma as a potassium chromate or dichromate solution gave no emission signal at 178.28 or 183.04 nm; emission was observed at 206.16 nm, however, owing to overlap with the chromium ion line at 206.15 nm.

The interference observed from copper(II) may be due to the reaction

$$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$$

This gives rise to free iodine vapour in the nebulizer chamber and a concentration of iodine in the gas–aerosol mixture supplied to the plasma, which exceeds that produced when an iodide solution is nebulized in the absence of an oxidant. The effect is similar to that observed in the direct determination of iodine by atomic absorption spectrometry when volatile iodine compounds are nebulized[5]. The small amount of copper(I) iodide formed produces a fine suspension (at the 100 p.p.m. level) and although the solution can still be nebulized, prolonged spraying eventually blocks the nebulizer. The interference effect observed at 206.16 nm corresponds to a spectral overlap with the copper line at 206.2 nm. Iron(III) also liberates iodine from aqueous iodide solution and so enhances the iodine emission signal. The same degree of enhancement is also observed with other oxidizing agents. The only interference observed at the iodine 178.28-nm line arises when phosphate is present; the enhancement observed is caused by spectral emission from the phosphorus 178.29-nm line. No spectral interference results from any of the ions investigated at the iodine 183.04-nm line.

Mercury. The presence of 50-fold (weight) amounts of Al, Ca, Cr(III), K, Mg, Na, Zn, NH_4, acetate, fluoride, nitrate or sulphate gave no interference with the emission signal produced by 10 p.m.m. of mercury introduced into the plasma as either mercury(I) or mercury(II) at both the 184.96- and 253.65-nm lines. Table II shows the effects produced by ions which interfered; these may all be attributed to spectral interference except for the effects observed with tin(II) and chloride. The interference from tin(II) on the signal observed for mercury(II) at both lines is due to its reduction to mercury(I) which, as described earlier, produces a more intense signal. The suppression of the emission intensity for mercury(I) observed in the presence of chloride is due to the precipitation of mercury(I) chloride. The filtered solution showed a suppression of signal, but when the precipitate was dissolved in excess of EDTA, no significant interference was observed.

Arsenic and selenium. The chemical form of arsenic or selenium does not appear to affect the final emission. The presence of 50-fold (weight) amounts of Al, Cu(II), Cr(III), Fe(III), K, Mg, Mn(II), Mo(VI), Na, NH_4, acetate, chloride, fluoride, iodide, nitrate, sulphate or phosphate produced no significant interference in the emission signal obtained with a 10-p.p.m. arsenic solution at 189.0, 193.69 and 228.81 nm. Spectral interferences were observed, however, for Co(II), Ni and Zn (Table II).

The presence of 50-fold (weight) amounts of Al, Ca, Co(II), Cu(II), Cr(III), Fe(III), K, Mg, Mn(II), Na, Ni, Zn, NH_4, acetate, chloride, fluoride, iodide, nitrate, sulphate or phosphate produced no significant interference in the emission signal obtained with a 10-p.p.m. selenium solution at 196.09 nm. Molybdenum(VI) produced a 10% enhancement in signal at this wavelength when present in 50-fold amounts.

DISCUSSION

Although with the experimental assembly available, the iodine non-resonance line at 206.16 nm yields a better detection limit than the 183.04- or 178.28-nm lines, it is not as useful in practice as the 183.04-nm line, owing to the severe spectral interferences observed from the transition metals, particularly zinc and chromium. The 183.04-nm line is the most suitable for the direct determinations, but the 206.16-nm line would probably be better for the determination of organically bound iodine in organic solvents.

This study has shown that the mercury 184.96-nm line provides a 30-fold improvement in detection limit compared to that obtained at 253.65 nm. The other great advantage of this line is its freedom from spectral interference. The detection limit of 1 p.p.b. may permit the direct determination of mercury in solutions produced from samples such as soils, rocks, urine and fish without the requirement of the commonly used cold vapour technique. The application of the plasma emission techniqe to the direct determination of traces of mercury in practical sample solutions is currently being studied.

The detection limits obtained for arsenic and selenium by this emission technique compare favourably with those obtainable by flame atomic absorption spectrometry. The arsenic 189.0-nm line appears to be the most useful, as no interferences were detected and the attainable detection limit was similar to that at the other lines. The disadvantage of this line is that purging of the monochromator is essential for sensitivity. The lines at 193.69 and 228.81 nm do not require purging of the monochromator to obtain satisfactory detection limits. The only spectral interference observed at 193.69 nm occurs with zinc, and this is only relatively slight; the 228.81-nm line suffers from spectral overlap with the cobalt and nickel lines and has the poorest detection limit of the three lines. Thus the choice of useful analytical lines lies between those at 189.0 and 193.69 nm; for most applications the former line appears more suitable. The determination of selenium is best performed at the 196.09-nm line, which gives the greatest sensitivity; the only interfering ion is molybdenum. Molybdenum does not interfere at the 203.99-nm line.

The results obtained indicate that the inductively coupled r.f. plasma forms an efficient cell for the atomization and excitation of relatively volatile elements. No chemical or physical interferences arising from solute vaporization effects were observed. The range of linearity of the calibration graphs obtained is in each case somewhat greater than would be expected. This may be attributed to the relatively low efficiency of the indirect nebulizer and expansion chamber employed; the atomic concentration in the plasma is therefore low and deviation from linearity in the working curves due to self-absorption is not observed until relatively concentrated solutions are nebulized. Although the extended linear range obtained in this way is given at the sacrifice of signal intensity, no significant improvement in signal-to-noise ratio (*i.e.* detection limit) is gained at the higher atomic concentrations produced in the plasma when the nebulization efficiency is increased. As an important potential application of the plasma source is to simultaneous multi-element analysis, the ability to produce an extended linear range for each element is important. Under these conditions it may then be possible to determine two or more elements simultaneously even when their concentrations, and their concentration ratios, in the sample solution differ greatly.

SUMMARY

The application of an inductively coupled high-frequency plasma source to the determination of iodine, mercury, arsenic and selenium by atomic emission spectrometry at wavelengths less than 200 nm is described. Optimal conditions have been established, and the spectral interference effects at different atomic lines for each element have been investigated. With the type of instrumentation employed, the determination of iodine at 183.04 nm, mercury at 184.96 nm, arsenic at 189.0 nm and selenium at 196.09 nm is recommended to minimize spectral interferences. No chemical or physical interferences resulting from the influence of foreign ions on the solute vaporization process have been noted.

RÉSUMÉ

Une méthode nouvelle par spectrométrie d'émission atomique est proposée et appliquée au dosage de l'iode, du mercure, de l'arsenic et du sélénium, à des longueurs d'onde inférieures à 200 nm. Les conditions optimales sont décrites. On examine également l'influence d'interférences spectrales, à différentes raies atomiqes pour chacun de ces éléments. On recommande les longueurs d'onde suivantes: 183.04 nm pour l'iode, 184.96 nm pour le mercure, 189.0 nm pour l'arsenic et 196.09 nm pour le sélénium. On ne note aucune interférence chimique ou physique d'ions étrangers.

ZUSAMMENFASSUNG

Die Anwendung eines induktiv gekoppelten Hochfreqenzplasmas auf die Bestimmung von Jod, Quecksilber, Arsen und Selen durch Atom-Emissionsspektrometrie bei Wellenlängen unterhalb 200 nm wird beschrieben. Die optimalen Bedingungen wurden festgestellt und die spektralen Störeinflüsse bei verschiedenen Atomlinien für jedes Element untersucht. Bei der verwendeten Art der instrumentellen Anordnung wird im Hinblick auf minimale spektrale Störungen die Bestimmung von Jod bei 183.04 nm, von Quecksilber bei 184.96 nm, von Arsen bei 189.0 nm und

von Selen bei 196.09 nm empfohlen. Chemische oder physikalische Störungen, die durch den Einfluss von Fremdionen auf den Verdampfungsvorgang der gelösten Substanz entstehen könnten, wurden nicht beobachtet.

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Analytica Chimica Acta, 64 (1973) 363–369

ATOMIC ABSORPTION AND FLUORESCENCE SPECTROMETRY WITH A CARBON FILAMENT ATOM RESERVOIR

PART XIII. THE DETERMINATION OF CHROMIUM WITH A FULLY ENCLOSED ATOM RESERVOIR

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A non-flame cell was used for chromium determinations by atomic absorption as early as 1961, when L'Vov[1] obtained an absolute sensitivity (1% absorption) of $1 \cdot 10^{-10}$ g at 425.4 nm in his graphite tube furnace. Later, a sensitivity of $2 \cdot 10^{-12}$ g was attained[2] at a wavelength of 357.9 nm. Fernandez and Manning[3] used a furnace of the "Massmann" type for the determination of chromium in natural water. This method gave a sensitivity of $2.6 \cdot 10^{-11}$ g and a detection limit of $4 \cdot 10^{-11}$ g. A "Mini-Massmann" furnace, consisting of a carbon rod with a hole drilled transversely through the centre, has given a sensitivity of $9.2 \cdot 10^{-12}$ g in aqueous solution[4], and $5 \cdot 10^{-12}$ g in the determination of chromium in petroleum products[5].

The method of Donega and Burgess[6], in which a sample is atomized from a tantalum boat in an inert atmosphere, yielded a sensitivity of $6 \cdot 10^{-12}$ g for chromium. A detection limit of $7 \cdot 10^{-11}$ g and a sensitivity of $2 \cdot 10^{-11}$ g have been obtained with a tungsten filament[7].

A carbon filament atom reservoir of the type developed by Alder and West[8] was used for the present study of the optimal parameters for chromium, and of various interferences.

EXPERIMENTAL

Apparatus

The modified Perkin-Elmer 290B atomic absorption spectrometer has been described previously[9]. The instrument was adapted for the measurement of transient signals by employing a fast-response d.c. system. The source was a "Rank Precision Industries" d.c.-operated hollow-cathode lamp, with a ceramic-shielded cathode. The output from the photomultiplier (IP 28) was connected to a storage oscilloscope (Telequipment, TD51) which incorporated a rapid-response "Type-K" amplifier.

The carbon filament used was a modification[10] of the previous design[8]; the effective length of the carbon filament was reduced from 25 mm to 10 mm, so that the filament was heated more quickly for a given applied voltage, and atomization of less volatile metals was facilitated. The filament assembly was enclosed in a glass chamber, fitted with a silica window to admit incident radiation. The chamber greatly extended the life of a filament by preventing the entrainment of air during vaporization of the sample. The field of view presented to the detector was limited by placing a metal disc containing a 0.5-mm pinhole mounted on the end of a cylindrical collimator (diameter 20 mm) behind the filament. The collimator tube protruded through a hole in the wall of the glass surround.

The cell was mounted on the instrument in the position normally occupied by the burner/nebulizer unit of the P.E. 290B spectrometer.

The hollow-cathode lamp was operated at a current of 18 mA (maximum recommended, 20 mA), and the monochromator entrance slit was adjusted to a bandpass of 0.7 nm.

Reagents

All reagents were of analytical grade, except some of those used in the interference studies. In such cases, a "blank" measurement was always carried out to ensure that no detectable amount of chromium was present in the reagents. The water used was glass-distilled and then deionized with a cation-exchange resin in the H^+ form.

Standard chromium solutions were prepared by dissolving the metal in perchloric acid to give a solution containing chromium(VI).

Measurement technique

A factor normally limiting the sensitivity of determinations on a carbon filament is that the liquid sample tends to spread along the filament, so that atoms are not concentrated in the field of view. However, chromium is sufficiently involatile to be placed onto a filament at such a temperature that spontaneous evaporation of the solvent occurs, without detectable loss of material by sputtering. In this way, all

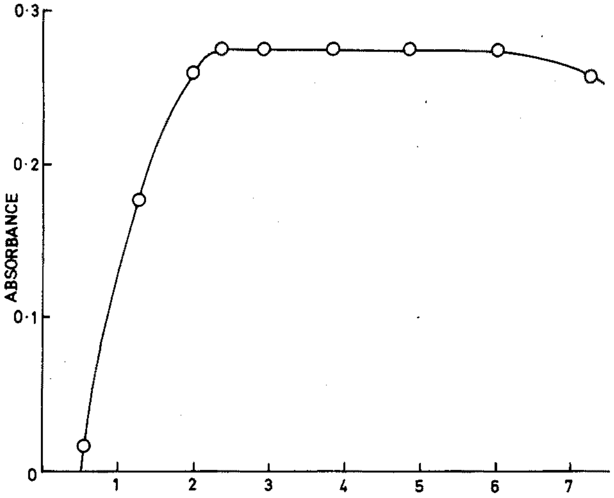

Fig. 1. Effect of nitrogen flow-rate on absorbance (1 ng Cr at 357.9 nm).

of the sample is concentrated into a very small area in the centre of the filament.

The monochromator was first tuned to the chromium line at 357.9 nm, the cooling-water supply to the electrodes was turned on, and the filament-sheathing gas flow was adjusted to the optimal setting. The aqueous sample (1 μl) was applied to a small recess in the filament by means of a Drummond micro-pipette, and in order to ensure good reproducibility by applying the sample at the correct temperature, the following procedure was strictly followed.

At time $t=0$ the filament voltage was switched on for about 1 s at 11 V and then switched off. This preconditioned the filament and its surroundings. At $t=30$ s, the power was switched on at 1 V. At $t=60$ s an aliquot (1 μl) of solution was delivered to the hot filament. The power was then switched off, the Variac was adjusted to 11 V, and the power was switched on for about 1 s to atomize the sample. This vaporization step was taken as $t=0$ for the next aliquot.

The height of the absorption peak was measured on the oscilloscope screen.

It was found that all of the sample was removed from the filament during the vaporization step, and thus there were no memory effects under normal conditions of usage.

RESULTS AND DISCUSSION

Limited field viewing

The height of the 0.5-mm pinhole with respect to the filament surface was varied, and it was found that the filament could be moved as far as about 0.5 mm below the level of the pinhole without serious loss in sensitivity. A steep temperature gradient is encountered above the filament surface, and above this position chromium atoms condense significantly to non-atomic species.

Effect of sheathing-gas flow-rate on signal

Nitrogen was used to provide an inert atmosphere around the filament. The flow-rate dependence curve for 1 p.p.m. chromium is shown in Fig. 1. It can be seen that any setting between 2.5 and 6.5 l min^{-1} was suitable. Much of the previous work on carbon filaments where an unenclosed cell was used, showed the sensitivity to be severely reduced at higher flow-rates. This was probably due to the entrainment of air by the sheathing gas, followed by combination of oxygen with the atomic species. With a fully enclosed cell, serious air entrainment is unlikely.

Effect of filament voltage on signal

The variation of absorbance with filament voltage for 1 p.p.m. chromium is presented in Fig. 2. Little improvement in signal was obtained above 11 V, and this setting was thus chosen for all measurements. Higher voltages led to premature ageing of the filament.

The half-life of the atomic absorption peak at this voltage was 0.17 s.

Calibration curves and detection limits

Chromium has at least eight resonance lines in the spectral range of the detector used in this work. Results obtained by previous workers have shown that

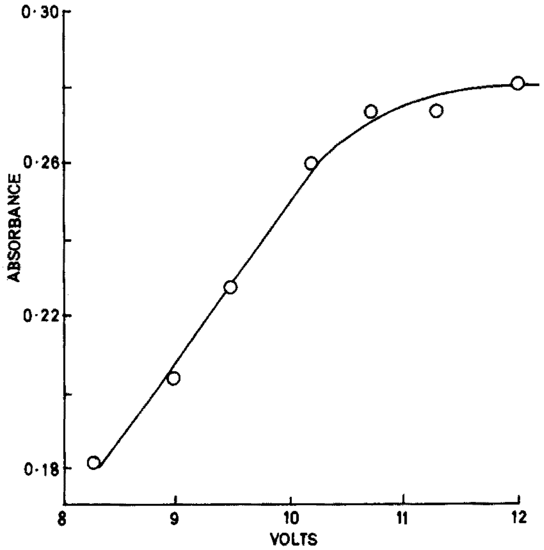

Fig. 2. Variation of absorbance with filament voltage (1 ng Cr at 357.9 nm).

the line at 357.9 nm is the most sensitive for atomic absorption measurements. This line, which originates from the ground state ($^7S_3$–$^7P_4^0$) was, therefore, used.

Several calibration curves were plotted at this wavelength; the useful working range extended to a concentration of about 2 p.p.m. chromium (1-μl aliquots), before non-linearity became too pronounced (Fig. 3). When the concentration reached 10 p.p.m., the line was almost parallel with the x-axis.

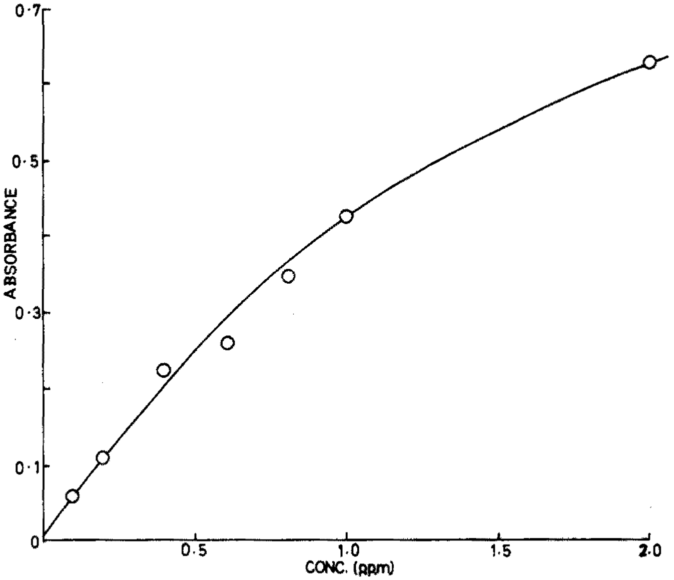

Fig. 3. Analytical calibration curve at 357.9 nm.

The sensitivity (1% absorption) and detection limit (signal: noise 2:1) were $9.2 \cdot 10^{-12}$ g and $1 \cdot 10^{-11}$ g, respectively. This detection limit is equivalent to a 1-µl aliquot of a 0.01 p.p.m. solution, and equals the lowest concentration normally detectable in a flame.

Reproducibility

Thirty replicate determinations were made under optimized conditions, with 1-µl aliquots of a 0.5-p.p.m. chromium solution. The relative standard deviation of the absorbance was 5.9%.

Origin of the signal

The possibility that the signals could be wholly or partly attributed to scatter was examined by studying a non-absorbing chromium line at 374.4 nm (originating from an energy level of 2.6 eV). No signal was observed at this wavelength, confirming that the signals at the 357.9-nm chromium absorbing line were due entirely to atomic absorption.

Interference studies

Previous work has shown that interferences with the carbon filament occur predominantly in the vapour phase[11] and that generally they are minimal immediately above the filament surface[9]. Thus, the 0.5-mm pinhole was arranged so that the bottom of the hole was just level with the filament surface.

Aliquots (1 µl) of a 0.5-p.p.m. chromium solution were used. Anionic species studied were chloride, nitrate and sulphate, and these were provided by the appropriate mineral acids. Concentrated hydrochloric acid ($4 \cdot 10^5$ p.p.m. Cl^-) and concentrated nitric acid ($7 \cdot 10^5$ p.p.m. NO_3^-) caused no interference, but 50% sulphuric acid ($5 \cdot 10^5$ p.p.m. SO_4^{2-}) suppressed the signal by *ca.* 30%. When the sulphuric acid was concentrated (almost 10^6 p.p.m. SO_4^{2-}), the interference was only slightly more pronounced. It is, therefore, possible to work with sulphuric acid solutions with only a moderate loss of sensitivity.

The effects of 20 cationic species were examined at concentrations of 5, 50 and 500 p.p.m. (10-, 100- and 1000-fold amounts, respectively). In every case (except vanadium), the anion was maintained constant by adding the metal as its chloride. The effects of these species are listed in Table I as percentage suppression of the absorbance of pure chromium (to the nearest 5%). Magnesium, lithium, sodium and potassium showed no interference at the above-mentioned levels.

It was previously suggested[9] that interferences occur largely because of physical occlusion of the analyte atoms by the concomitant species in the gas phase, and results obtained during nickel studies[9] tended to confirm this. It would thus be expected that those species of volatility similar to chromium, *i.e.* those which would be simultaneously present in the field of view, would interfere the most. It can be seen from Table I that metals such as iron, cobalt and calcium (similar volatility to chromium) show greater interference than metals such as Mg, Li, Na and K, and this is in agreement with the above hypothesis. However, many anomalies are present. Some metals show more interference than expected (*e.g.* Sr, Ca and Ba), whilst others interfere less (*e.g.* Ti, V and Mn).

It is obvious, therefore, that other factors also influence interference effects,

TABLE I

PERCENTAGE SUPPRESSION OF ABSORBANCE OF 0.5 p.p.m. (0.5 ng) CHROMIUM BY ADDITION OF INTERFERING SPECIES

(Sample volume = 1 μl)

Diverse ion[a]	*Interference (%)*		
	5 p.p.m.	*50 p.p.m.*	*500 p.p.m.*
Sr	15	30	80
Fe(III)	10	30	75
Co(II)	15	45	60
Cu(II)	0	15	75
Ca	0	20	40
Ba	0	20	30
Al	5	10	35
Sn(II)	0	10	20
Sb	0	5	20
Rb	0	5	20
Ti(IV)	0	5	10
Pb	0	0	20
Mn(II)	0	0	10
Zn	0	0	5
Hg(II)	0	0	5
V(V)	0	0	0

[a] All were added as the chloride salt, except antimony (Sb_2O_3 in HCl) and vanadium (NH_4VO_3 in HCl).

and it is possible that these are of a chemical as well as a physical nature. Further work on this topic is in progress.

We are grateful to Laporte Industries Ltd., for assistance and support for this programme and to the S.R.C. for the provision of a CAPS award for K.W.J.

SUMMARY

The detection and measurement of chromium by atomic absorption spectrometry with a carbon filament atom reservoir is described. At a wavelength of 357.9 nm, a sensitivity (1% absorption) of $9.2 \cdot 10^{-12}$ g was obtained. The detection limit was $1 \cdot 10^{-11}$ g; in terms of concentration this is similar to that normally detectable in a flame. Results are presented for the effects of a number of interfering species.

RÉSUMÉ

On décrit une méthode spectrométrique par absorption atomique pour déceler et doser le chrome, en utilisant un réservoir atomique à filament de carbone. La sensibilité est de $9.2 \cdot 10^{-12}$ g (absorption 1%), à la longueur d'onde de 357.9 nm. La limite de détection de $1 \cdot 10^{-11}$ g correspond à celle obtenue normalement, avec flamme. On examine l'influence de diverses interférences.

ZUSAMMENFASSUNG

Der Nachweis und die Bestimmung von Chrom durch Atomabsorptionsspektrometrie unter Verwendung einer Graphitstab-Küvette werden beschrieben. Bei der Wellenlänge 357.9 nm wurde eine Empfindlichkeit (1% Absorption) von $9.2 \cdot 10^{-12}$ g erhalten; dies entspricht etwa der üblicherweise in einer Flamme nachweisbaren Konzentration. Die Ergebnisse für die Einflüsse störender Spezies werden vorgelegt.

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Analytica Chimica Acta, 64 (1973) 371–379

THE DETERMINATION OF MOLYBDENUM IN SEA WATER BY HOT GRAPHITE ATOMIC ABSORPTION SPECTROMETRY AFTER CONCENTRATION ON *p*-AMINOBENZYLCELLULOSE OR CHITOSAN

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The hot graphite atomizer for atomic absorption spectrometry seems to be widely applicable in oceanographic analysis, especially for the determination of those elements, *e.g.* molybdenum, for which the sensitivity in flames is not very good.

Molybdenum has so far been determined in waters by other analytical methods, a critical evaluation of which was published several years ago[1]; these methods were colorimetry on organic extracts, emission spectrography and conventional atomic absorption spectrometry. Data on molybdenum in geological and biological samples have been obtained with an Autoanalyzer[2]; no preconcentration was needed to determine molybdenum colorimetrically in sea water by means of its catalytic action on the iodide–peroxide reaction.

Molybdenum in sea waters has also been determined colorimetrically after separation procedures involving iron hydroxide flotation[3], chromatography on the chelating resin Dowex A-1[4,5] and on diethylaminoethylcellulose in the thiocyanate form[6]. These uses of a chelating polymer were based on preconcentrations of molybdenum from acidified sea water; a separate sample of sea water was required for the determination of the Group VI B elements, because other metal ions are quantitatively collected on the polymer at higher pH[4].

A better approach is to select a polymer which shows reasonable selectivity towards molybdenum in order to reduce the column and eluate volumes, and to avoid addition of reagents to the samples, and unnecessary washings; thus only a small fraction of a sample is needed for the molybdenum determination.

The exceptional efficiency of chitosan in collecting vanadium, chromium, molybdenum and tungsten has been described[7], and was explained in terms of a particular interaction of the oxyanions with the amino groups of chitosan at pH values where homo- or hetero-poly derivatives can be formed. This interaction is stronger than the similar interaction of molybdenum and tungsten with diethylaminoethylcellulose (DEAEC), as would be expected on the basis of the lower number of amino groups available on DEAEC.

Molybdenum and tungsten can be collected on DEAEC in the thiocyanate form from 0.02 *M* ammonium thiocyanate at pH 3.0, while rhenium, which does not form poly derivatives, is not; molybdenum can be eluted with 0.1 *M* ammonium thiocyanate at pH 5.0, while tungsten can be eluted with 0.1 *M* sodium hydroxide–0.1 *M* chloride solution[8]. Data on the behaviour of molybdenum in paper partition chromatography in thiocyanic acid indicate high R_F values at pH 3.0[9,10]. As the paper was natural cellulose, this indicates the essential role of the diethylaminoethyl groups of DEAEC in retaining molybdenum in thiocyanate solutions at low pH.

p-Aminobenzylcellulose has been studied in organic media, and from the data obtained[11–14] it is predictable that it should be selective toward molybdenum, while permitting simple elution.

In practice, it is possible to combine molybdenum isolation on a chelating polymer with the hot graphite atomic absorption spectrometry in two ways: determination of molybdenum in a small eluate whose chemical composition does not disturb the atomic absorption, or in the polymer as a solid with the help of a baseline corrector to avoid light absorption by smokes.

EXPERIMENTAL

Polymers

p-Aminobenzylcellulose (Bio-Rad, California), microgranular diethylaminoethylcellulose (Whatman) and chitosan[14] were used.

Solutions

Chlorides and nitrates were used, except for antimony tartrate, potassium chromate, sodium arseniate and sodium molybdate, the pH was adjusted with hydrochloric acid. Molybdenum solutions were 1 p.p.m. in triple distilled water. The other solutions were 0.44 m*M* or 1 p.p.m. For the distribution experiments, 200 mg of polymer in 50 ml of solution were shaken in a Dubnoff machine at 1000 rev $\min^{-1}$ and 21°. For the precipitation experiments, the chitosan solution in acetic acid (1+9) contained 20 mg chitosan per ml. The molybdate solution in acetic acid (1+9) contained 55 mg Mo ml^{-1}.

The procedure for the above tests was as follows: 5 ml of molybdenum solution, 5 ml of the second ion (1 m*M*) solution and 5 ml of 1 *M* ammonium thiocyanate were mixed and added dropwise to a 25-ml portion of the chitosan solution with stirring. After 10 min of stirring and centrifuging, a portion of the liquid was pipetted for analysis.

Samples

Surface sea water was collected a few km offshore from Capo Conero (Ancona, Italy), and was filtered on a 0.45-μm Millipore membrane mounted on a Teflon suppport. It was then stored in the refrigerator for up to 2 weeks. Concentrated hydrochloric acid was used to adjust the pH to 2.5 before the water was passed through the columns.

Columns

Columns were 3 × 1 cm and contained 0.5 g of polymer. After the sea water had been passed, they were washed with 15 ml of triple distilled water. For the elution of molybdenum from the *p*-aminobenzylcellulose columns, some 1 *M* ammonium carbonate solution was introduced to imbibe the whole column and left for 3 h; then the flow-rate was resumed and three 5-ml portions of 1 *M* ammonium carbonate solution were collected.

Instruments

A Perkin-Elmer 305 atomic absorption spectrophotometer, equipped with a HGA-70 graphite atomizer or a three-slot air–acetylene burner, a Perkin-Elmer baseline deuterium corrector, and a Hitachi Perkin-Elmer 56 recorder were used. U.P.P. nitrogen was generally used as purging gas for the graphite atomizer, but some measurements were also done with argon. The HGA-70 program normally adopted for molybdenum was No. 7 with 10 V and 30, 30, 15 s, for a 20-μl sample introduced with an Eppendorf pipette. Care must be taken to have an atomization period long enough to permit a thorough cleaning of the tube.

RESULTS AND DISCUSSION

Collection of molybdenum

When the data on the collection of several elements (Table I) are com-

TABLE I

COLLECTION OF ELEMENTS (%) ON CHITOSAN AND CELLULOSES

(200 mg were used with 50 ml of 0.44 m*M* solutions at pH 2.5 and 6.0. Molybdenum solution, 1 p.p.m. Data for 0.01 *M* EDTA solutions are also reported to assess the strength of the metal–polymer interaction)

pH		*Time (h)*	*Cr(III)*	*Cr(VI)*	*Mn*	*Fe*[a]	*As*	*Mo*	*Ag*	*Sn*	*Sb*	*Hg*	*Pb*
COitosan													
	Alone	1	17	81	21	28	100	100	80	17	38	98	26
2.5		12	54	98	20	23	73	100	96	96		100	48
	EDTA	1	28	70	16	16	27	—	43	—	16	58	13
	Alone	1	38	12	9	79	25	0	—	—	—	100	95
6.0		12	—	18	26	65	73	—	—	—	—	100	99
	EDTA	1	21	36	26	2	11	—	—	—	—	89	2
Diethylaminoethylcellulose													
	Alone	1	58	85	8	14	10	100	23		37	72	5
2.5		12	13	80	2	0	100	100	95	100		72	0
	EDTA	1	20	41	7	6	0	—	15		6	32	0
	Alone	1	65	89	33	71	90	100	—	—	—	30	86
6.0		12	—	98	13	38	100	100	—		—	72	98
	EDTA	1	21	19	22	0	4	—	—	—	—	35	0
p-Aminobenzylcellulose													
	Alone	1	5	38	3	3	0	83	27		11	7	0
2.5		12	10	35	5	6	0	91	28		15	10	0
	EDTA	1	21	12	0	6	0	—	16		2	8	0
	Alone	1	30	33	15	19	0	87	—	—	—	21	24
6.0		12	30	30	5	15	0	95	—	—	—	20	12
	EDTA	1	5	11	18	2	0	—	—	—	—	0	0

[a] The corresponding data for Ni, Cu and Zn will be published elsewhere.

pared, the good selectivity of *p*-aminobenzylcellulose becomes evident. Most elements are not collected on this cellulose under appropriate conditions, except chromium to a limited extent.

Diethylaminoethylcellulose and chitosan are less selective than *p*-aminobenzylcellulose, as they collect many other elements with high efficiency, and their reaction with molybdenum is faster than that for *p*-aminobenzylcellulose. It should be pointed out that chitosan does not collect molybdenum appreciably at high pH, but it is difficult to elute molybdenum with carbonate from chitosan.

Diethylaminoethylcellulose collects less Mn, Fe, Zn at pH 6.0 and chromium(III) at pH 2.5 after 12 h than after 1 h: this trend can be interpreted as an indication of relatively weak interactions of these cations with the cellulose in aqueous solution; with chitosan, this happens only for iron. The data for collection of mercury(II) on the three celluloses can be taken as an example of the order of affinity that these polymers exhibit for metal ions in aqueous solution.

The extremely strong fixation of molybdenum to chitosan that takes places in all acidic media including acetic and formic acids, occurs even in the presence of a very large amount of thiocyanate. While most other elements are kept in solution nearly quantitatively by the complexing action of thiocyanate (Table II), molybdenum is quantitatively carried down by chitosan (*cf.* ref. 7). Some mercury(II) accompanies molybdenum because of the slight solubility of mercury(II) thiocyanate.

TABLE II

SEPARATION OF 275 mg OF MOLYBDENUM FROM OTHER IONS

(Precipitation of chitosan polymolybdate in 40 ml of a 0.125 *M* thiocyanate solution at pH 3.8. Washing with 10 ml of 0.125 *M* ammonium thiocyanate. Measurements by a.a.s.)

Diverse ion	*Amount (μg)*			*% Left in solution*
	Added	*Found in solution*	*Found in washings*	
Cu(II)[a]	318	292	0	92
Pb(II)[a]	1036	996	0	96
Ni(II)[a]	294	228	6	80
Cd(II)[a]	560	518	0	94
Ti(III)[a]	240	143	50	80
Co(II)	294	268	26	100
Fe(III)	225	156	17	77
Hg(II)	1003	630	70	68
Zn(II)	326	325	0	100
Cr(III)	260	52	10	24
Mg(II)	121	121	0	110
Ca(II)	200	200	0	100
Al(III)	125	120	5	100
UO_2^{2+}[b]	1000	870	130	87
PO_4^{3-}[b]	1000	0	0	0

[a] Results confirmed by standard polarographic methods.

[b] Results obtained by radiochemical measurements with labelled chemicals (^{32}P-phosphate and ^{233}U-uranyl nitrate).

Chromium can be better separated under different conditions. Obviously, it would be impossible to elute molybdenum from chitosan with thiocyanate solutions, and this was experimentally confirmed on 3 × 1 cm columns.

Great elution difficulties are also encountered with the other celluloses, when thiocyanate is used. Earlier workers conditioned diethylaminoethylcellulose in the thiocyanate form before introducing molybdenum, so that the extent of the interaction would be limited by a slow kinetic mechanism, but without preliminary conditioning, molybdenum cannot be eluted. For example, when 2.5 or 5.0 μg of molybdenum in 50 ml of chloride-containing solution at pH 2.5 was passed through a *p*-aminobenzyl- or diethylaminoethyl-cellulose column, and elution attempted with 0.1 *M* thiocyanate, only traces of molybdenum appeared in 20 ml of eluate.

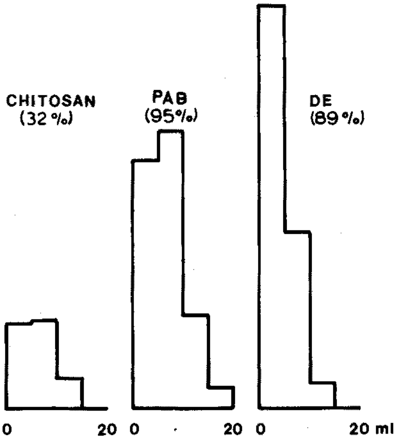


Fig. 1. Elution curves of 5.0 μg of molybdenum from chitosan, DE and PAB in 1 × 3 cm columns, with 1 *M* ammonium carbonate.

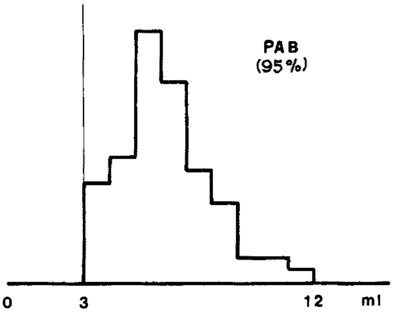


Fig. 2. Elution curve of molybdenum after passing 50 ml of sea water through a 1 × 3 cm PAB column, with 1 *M* ammonium carbonate.

However, ammonium or sodium carbonate solutions eluted molybdenum quantitatively from *p*-aminobenzylcellulose and partially from DE and chitosan (Figs. 1 and 2). As carbonate and thiocyanate solutions do not affect the atomization in the graphite furnace, the calibration graphs were found to be linear up to a concentration of 300 μg Mo l^{-1}.

Application to sea water

Preliminary experiments with 2.5 or 5.0 μg of molybdenum in 50 ml of a 3% sodium chloride solution showed that good results were to be expected from the application of this procedure to sea water.

In the light of the above-described interaction of molybdenum with these polymers, it was expected that a standard addition technique with the collection method would be applicable in the case of molybdenum with no doubts. It is known that certain metal ions, *e.g.* zinc, when added to sea water, do not go into equilibrium with the naturally occurring chemical forms, so that a spike may not

TABLE III

DETERMINATION OF MOLYBDENUM IN SEA WATER

(pH 2.5, with 3 × 1 cm columns of *p*-aminobenzylcellulose after elution with 1 *M* ammonium carbonate)

% Absorption readings						*μg Mo l^{-1} found in sea water*
5-ml elution fractions				*Total*	*Standard (2.5 μg Mo in 5 ml)*	
1	*2*	*3*	*4*			
100-ml sample + 1.0 μg Mo						
68	58	9	0	135[a]	165[b]	10.5
250-ml sample + 2.5 μg Mo						
102	114	0	0	206	100[c]	10.6
250-ml sample						
19	86	5	0	110	100[c]	11.0
500-ml sample						
80	126	0	0	214	100[c]	10.7

[a] The values higher than 100% absorption mean that the sample was diluted for analysis.

[b] 1/5 scale expansion.

[c] 1/10 scale expansion.

be representative of the total element actually present in the sample. The data obtained for molybdenum are given in Table III.

Recommended procedure for sea waters

Prepare a column with 0.5 g of *p*-aminobenzylcellulose in distilled water in a 50-ml burette. Percolate 50 ml of acidified sea water at pH 2.5 and wash with 15 ml of water (until a negative silver chloride test is obtained); then add 1 *M* ammonium carbonate solution, leave for 3 h, resume the flow-rate and collect three 5-ml portions of 1 *M* ammonium carbonate. For 3-h standing the yield is 80%, while for 15-h standing, it is between 95 and 100%.

It should be mentioned that the first eluate fraction appears slightly yellow; this is due to the action of carbonate on *p*-aminobenzylcellulose and cannot be avoided by any pretreatment or washing. When atomic absorption spectrometry with the graphite furnace is done on these samples, smoke is recorded as soon as the charring period is switched on, but there are no interferences from smoke during the atomization period for two reasons: (*a*) the scale expansion is moderate for the above conditions involving about 0.5 μg of molybdenum (which is usually present in 50 ml of sea water); (*b*) the atomization signal of molybdenum appears at least 1 s after the beginning of the atomization period, so that it can be distinguished from the smoke. The readings for eluate fractions are shown in Fig. 3.

Chitosan and *p*-aminobenzylcellulose give rise to little smoke, compared to Dowex A-1 (Fig. 4). All these backgrounds can be corrected by the Perkin-Elmer Deuterium Corrector, and therefore molybdenum can also be determined on the polymer itself after washing and homogenizing. In fact, the ratio 0.5 μg of molyb-

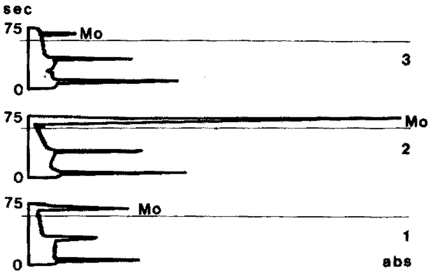
TABLE IV

A COMPARISON OF METHODS FOR THE DETERMINATION OF MOLYBDENUM IN SEA WATER

	Proposed method		*Dowex A-1*[a]	*Dowex 1-X8*[b]	*Dowex 1-X8*[b]
	Chitosan	*PAB*			
Amount (g)	0.5	0.5	—	10.0	10.0
Column conditioning	None	None	Nitrate	Chloride	Thiocyanate
Column dimensions (cm)	1 × 3	1 × 3	1 × 6	2.5 × 3.5	2.5 × 3.5
Sea water volume (ml)	50	50	3000	1000	1000
pH adjustment	2.5	2.5	5.0	0.1 M HCl+6% H_2O_2	0.1 M HCl+0.1 M SCN^-
Washing (ml)	15 water	15 water	200 water	50, 0.5 M NaCl	100, 1 M H_2SO_4
Eluate (ml)	None	10 $(NH_4)_2CO_3$ 1 M	24 NH_4OH 2 N	60, 0.5 M NaOH +0.5 M NaCl	60, 0.5 M NaOH +0.5 M NaCl
Further treatments (extractions, etc.)	None	None	Required	Required	Required

[a] Riley and Taylor[4].

[b] Kawabuchi and Kuroda[5].



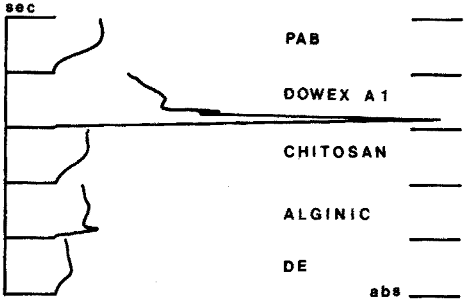


Fig. 3. Readings for the three 5-ml eluate fractions, showing no interferences by smokes. 0.25 μg Mo total; 20-μl samples; chart speed 20 mm min^{-1}.

Fig. 4. Readings of 10-mg samples of various polymers during the atomization period, at the 313.2-nm wavelength for molybdenum. No deuterium background compensation. Chart speed 100 mm min^{-1}.

denum in 0.5 g of polymer is more favorable than 0.5 μg of molybdenum in 5 ml, for a sampling of 20 mg of polymer or 20 μl of solution, respectively.

Conclusions

The method presented compares favourably with other methods available for the determination of molybdenum in sea water. When ten determinations were done on aliquots of one sea water sample, the mean value was found to be 10.42 μg Mo ml^{-1} with a standard deviation of ±0.13 μg.

The columns are small and do not require conditioning, the sea water volume is very small and no chemicals need be added except for the acid for the pH adjustment; elution is optional and much simpler. A comparison of methods is given in Table IV.

This method can be easily applied to routine determinations on large numbers of samples with limited glassware and personnel.

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SUMMARY

A comparative study of the chelating ability of chitosan, *p*-aminobenzylcellulose and diethylaminoethylcellulose, for a number of metal ions is discussed. There is a strong interaction between molybdenum and these polymers in thiocyanate solutions and in sea water. By combining the sensitivity of graphite-furnace atomic absorption spectrometry with the efficiency of the selective collection of molybdenum on *p*-aminobenzylcellulose or chitosan at pH 2.5, it was possible to determine molybdenum in as little as 50 ml of sea water.

RÉSUMÉ

Une étude comparative est effectuée sur le pouvoir chélatant de divers polymères, chitosane, *p*-aminobenzylcellulose et diéthylaminoéthylcellulose, pour un certain nombre de métaux. On observe une forte interaction entre le molybdène et ces polymères, en milieu thiocyanate et dans l'eau de mer. On propose une méthode pour le dosage du molybdène dans des échantillons d'eau de mer ne dépassant pas 50 ml.

ZUSAMMENFASSUNG

Eine vergleichende Untersuchung der Chelatisierungsfähigkeit von Chitosan, *p*-Aminobenzylcellulose und Diäthylaminoäthylcellulose gegenüber einer Anzahl von Metallionen wird diskutiert. Eine starke Wechselwirkung tritt zwischen Molybdän und diesen Polymeren in Thiocyanatlösungen und in Meerwasser auf. Durch die wirksame, selektive Anreicherung von Molybdän an *p*-Aminobenzylcellulose oder Chitosan bei pH 2.5, anschliessende Elution mit Carbonat und Atomabsorptionsspektrometrie unter Verwendung einer Graphit-Heizvorrichtung war es möglich, Molybdän in nur 50 ml Meerwasser zu bestimmen.

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FLAMELESS ATOMIC ABSORPTION SPECTROMETRY OF ANTIMONY

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The flameless atomic absorption spectrometry of volatile and involatile elements has been widely investigated[1] because of the high absolute sensitivity which permits the use of very small samples; the reliability of the technique is comparable with that of the conventional flame method. However, no published information exists pertaining to the determination of antimony by flameless atomic absorption spectrometry.

This paper describes the atomic absorption behavior of antimony with a carbon rod atomizer and its application to metallurgical samples.

EXPERIMENTAL

Apparatus

A Varian Techtron AA-1000 atomic absorption spectrophotometer was used with a Varian Techtron Model 61 carbon rod atomizer substituted for the burner assembly. The atomic absorption signals were recorded on a Hitachi QPD-54 recorder. The carbon rod was of the "Mini-Massmann" type which had a 1.5-mm diameter transverse hole as the sample cavity. Light from the hollow-cathode lamp was focussed through the cavity and the absorption was measured. Argon was used as the inert gas. A Hitachi hollow-cathode lamp was operated at 7 mA to give the optimal absorption. A 5-μl syringe (S.G.E. Pty Ltd., Australia) was used to inject samples into the carbon rod. The 206.8- and 217.6-nm lines were compared for measuring antimony absorption. The line at 206.8 nm showed a little higher background noise than that at 217.6 nm, and the latter was therefore used.

Reagents

Standard antimony solution was prepared from potassium antimonyl tartrate. All reagents were of analytical grade. Organic solvents were purified by distillation.

Procedure

A 0.5-μl sample was syringed into the rod. The sample was preheated (dried and ashed) and atomized by heating with a unit requiring a maximum input of 3 kW at 110 V a.c. The optimal conditions for measuring the atomic absorption of antimony were as follows: drying 0.7 V for 20 s (rod temperature *ca.* 60°); ashing 1.8 V for 30 s (rod temperature *ca.* 180°); atomization 5.6 V for 3 s (rod temperature *ca.* 2200°).

RESULTS AND DISCUSSION

Effect of rod temperature on antimony absorption

The antimony analytical signal varied with the rod temperature. This relationship is shown in Fig. 1. Measurements of the rod temperature were carried out with an optical pyrometer. Increasing temperature resulted in the absorption peaks becoming narrower and higher. However, peak-area measurement proved to be constant above 1500°. Therefore, peak-area measurement is recommended. No antimony signal was observed when the rod temperature was applied for a second time.

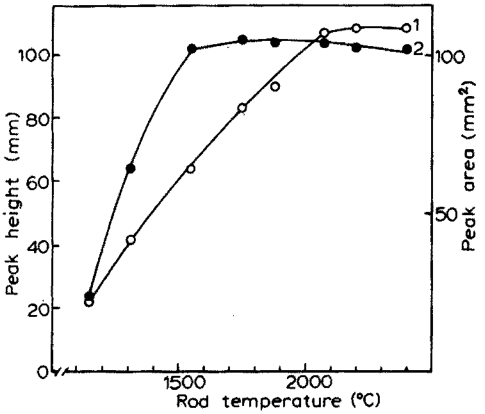

Fig. 1. Effect of rod temperature on atomization of antimony. 1 = Peak-height measurement; 2 = peak-area measurement. Antimony taken 2.5 ng (0.1 *M* HCl).

Effect of inert gas flow-rate

The flow of inert gas was from the tubing beneath the carbon rod; argon was used as the inert gas. Variations in argon flow-rate between 0.5 and 3.5 l min^{-1} had negligible effects. However, the flow-rate of argon was maintained at 2 l min^{-1}.

Effect of spectral band width on antimony absorption

The effect of spectral band width for the measurement of the antimony absorption at 217.6 nm is shown in Fig. 2. The optimal spectral band width at 217.6 nm was 0.2 nm.

Detection limit

With the optimal conditions defined above, the detection limit and sensitivity were determined at 217.6 nm. The limit of detection with this device for a 0.5-μl sample was 10^{-10} g. The sensitivity (for 1% absorption) was 10^{-12} g.

To ascertain the origin of the absorption signals, the non-absorbing antimony line at 217.93 nm was chosen as being close to the absorbing line. In this case no

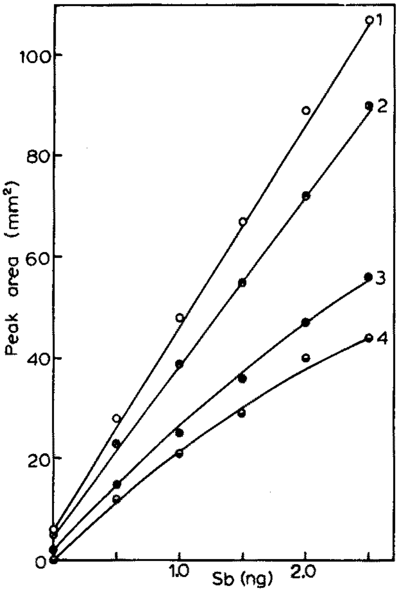

Fig. 2. Effect of spectral band width on antimony absorption. 1 = 0.2 nm; 2 = 0.5 nm; 3 = 1.0 nm; 4 = 2.0 nm. Absorption measured at 217.6 nm. Sample volume of antimony: 0.5 μl (0.1 *M* HCl).

signal was observed, showing that the signals at the antimony absorbing lines originated purely from atomic absorption by antimony.

Reproducibility

Aliquots (0.5 μl) of a 2.4 μg ml^{-1} solution of antimony were repeatedly analyzed under optimal conditions. Five determinations gave a relative standard deviation of 3%. The reproducibility of the absorption in the presence of matrix elements was a little poorer than that for pure antimony solutions. Solutions containing antimony and 100-fold (molar) amounts of lanthanum were tested. The relative standard deviation was 4%.

Interferences

The effects of diverse metals on the antimony absorption signal were measured. Solutions (0.02 m*M*) of antimony containing 100-, 1000- or 2000-fold (molar) amounts of different foreign ions were employed. The results obtained are shown in Table I. The cations tested were added as their chlorides or nitrates; the effects of the interferences are listed as recovery of antimony. Silver, chromium, vanadium and molybdenum showed significant suppression of antimony absorption at the 100-fold level, while aluminium and calcium produced no interferences even at the 1000-fold level. Copper interference was serious at the 1000-fold level and above. Hydrochloric and nitric acids did not alter the antimony absorption in concentrations of less than 0.1 *M*. The effect of higher concentration of acids was not tested because of corrosion of microsyringe. Jackson and West[2] attempted to correlate the degree of interference with some physical properties of the interfering species for nickel, and demonstrated that some correlations were evident; elements of low volatility, *i.e.* similar volatility to

TABLE I

EFFECT OF FOREIGN IONS ON ANTIMONY ABSORPTION

(Sample volume, 0.5 μl of 0.02 m*M* antimony solution, corresponding to 1.2 ng Sb. Drying, 60° for 20 s; ashing, 180° for 30 s; atomization, 2200° for 3 s; measured at 217.6 nm)

Foreign ion[a]	*mM*	*Recovery of antimony (%)*	*Foreign ion*[a]	*mM*	*Recovery of antimony (%)*
Na	2	93	V	2	76
Pb	2	104	Mo	2	82
Ag	2	84	La	2	100
Cd	2	96	Ca	20	103
Al	2	97	Cu	2	100
	20	101		20	70
Cr	2	89		40	54

[a] Hydrochloric acid or nitric acid solution (0.1 *M*) used.

nickel, tended to interfere the most. However, the nature of the interferences was uncertain for antimony.

Measurement combined with extraction

The application of solvent extraction is attractive in atomic absorption spectrometry for the elimination of interferences. In the flameless method, solvent extraction has proved effective for the determination of various trace elements without matrix effects. The following extraction systems for antimony were compared: chloride[3], tri-*n*-butyl phosphate (TBP)[4] and diethyl dithiocarbamate (DDTC)[5]. Methyl isobutyl ketone was used as organic solvent for the chloride and DDTC complex systems, while toluene was used for the TBP system. All extractions were carried out with 10 ml of organic solvent from 20 ml of aqueous antimony solutions. Calibration curves for the extraction methods are shown in Fig. 3. The TBP and DDTC complex extractions showed much lower sensitivity than the chloride extraction. In all cases the extractability of antimony was good; the lower sensitivities for the TBP and DDTC complexes may be caused partly by the effects of different viscosity of the extracts in delivery into the rod, and partly from the formation of some involatile compounds in preheating. However, the origin of the lower absorption for the TBP and DDTC complex extracts is not known with certainty at the present time.

APPLICATIONS

The flameless atomic absorption method was applied for the determination of antimony in metallurgical samples. Solvent extraction was essential because of matrix effects on the antimony absorption.

Procedure

Dissolve 0.5–1 g of sample in 5 ml of aqua regia. Warm gently on a steam-bath to ensure complete dissolution. Cool and dilute to 100 ml with 6 *M* hydrochloric acid in a volumetric flask. Transfer the aliquots (less than 50 μg Sb) to a separatory

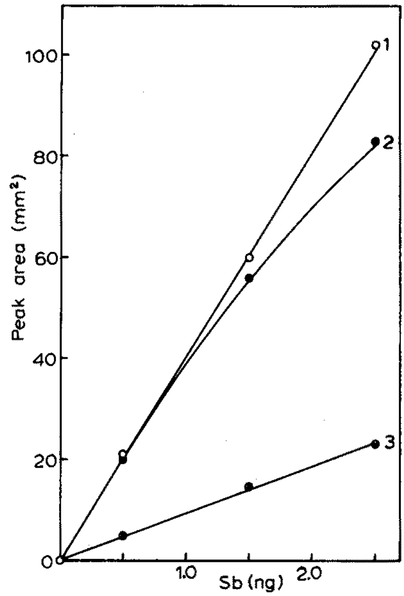

Fig. 3. Antimony calibration curves. 1 = Chloride extraction (in MIBK); 2 = DDTC complex extraction (in MIBK); 3 = TBP extraction (in toluene).

funnel and add enough hydrochloric acid to make the concentration 6 *M* when the solution is diluted to 20 ml. Add 0.5 ml of 5% (w/v) sodium nitrite solution and dilute to 20 ml. Shake the resultant solution for 1 min to oxidize antimony to the pentavalent state. Then extract antimony in 10 ml of methyl isobutyl ketone by shaking for 3 min. Place the aliquot of the organic phase by means of a syringe into the rod and then atomize the sample after drying and ashing. Record the antimony absorption at 217.6 nm. Prepare a calibration curve by extracting antimony from standard solutions of antimony.

TABLE II

DETERMINATION OF ANTIMONY IN SELECTED SAMPLES

Sample	*Sb added (%)*	*Sb found (%)*		
		Proposed method	*Flame method*[3]	*Certified value*
Aluminium alloy[a]	—	0.049, 0.051	0.043	0.05
(BCS 216/1)	0.037	0.086, 0.084		
Copper alloy[b]	—	0.22, 0.21	0.24	0.24
(BCS 183/1)	0.20	0.41, 0.42		
Crude copper[c]	—	0.066, 0.064	0.066	0.064[d]
	0.037	0.103, 0.105		

[a] 0.73% Mn, 0.74% Mg, 0.40% Fe, 0.10% Ti, 0.11% Zn, 0.05% Pb, 0.05% Sn, 0.06% Ni.
[b] 5.17% Zn, 5.01% Sn, 3.51% Pb, 0.51% Ni, 0.14% As, 0.51% P.
[c] 0.14% Ni, 0.08% Pb, 0.05% As, 0.005% Fe, 0.001% Zn, 0.001% Mg.
[d] Polarographic.

Results of determinations on selected samples

The results of the determination of antimony in selected samples are presented in Table II. These results indicate that antimony can be determined with good accuracy, and that flameless atomic absorption spectrometry can be applied successfully to the analysis of metallurgical samples provided that the atomic absorption measurement is combined with solvent extraction.

The authors express their thanks to Nippon Electric Varian Ltd. for the loan of apparatus.

SUMMARY

Flameless atomic absorption spectrometry of antimony has been investigated with a carbon rod device. Antimony may be determined in solution at a level of 10^{-10} g with a sample volume of 0.5 μl. Optimal conditions and interferences are described. Matrix effects on antimony necessitated a preliminary solvent extraction of the chloride complex from hydrochloric acid solution containing nitrite with methyl isobutyl ketone. The determination of antimony in metallurgical samples was shown to be satisfactory.

RÉSUMÉ

Une recherche est effectuée sur la spectrométrie par absorption atomique sans flamme de l'antimoine. On arrive à doser 10^{-10} g avec un volume d'échantillon de 0.5 μl. On examine les conditions optimales et les interférences. L'influence de la matrice sur l'antimoine nécessite une extraction préliminaire dans un solvant. Cette méthode est appliquée avec succès au dosage de l'antimoine dans des échantillons métallurgiques.

ZUSAMMENFASSUNG

Die flammenlose Atomabsorptionsspektrometrie von Antimon unter Verwendung einer Graphitstab-Anordnung wurde untersucht. 10^{-10} g Antimon kann in Lösung bei einem Probenvolumen von 0.5 μl bestimmt werden. Die optimalen Bedingungen und die Störungen werden angegeben. Matrixeinflüsse auf die Bestimmung von Antimon machten es notwendig, vorher den Chloridkomplex aus salzsaurer, nitrithaltiger Lösung mit Methylisobutylketon zu extrahieren. Die Bestimmung von Antimon in metallurgischen Proben führte zu zufriedenstellenden Ergebnissen.

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ATOMIC ABSORPTION INHIBITION TITRATION OF ORTHOPHOSPHATE AND POLYPHOSPHATES*, **

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Despite the large literature on chemical inhibition effects in atomic absorption and emission spectroscopy, few workers have exploited this effect for the determination of the inhibiting anions. Flame emission inhibition measurement of anions was first applied by Dippel *et al.*[1]. Since then work has also been done in both absorption and emission by other investigators[2–7], but sensitivity is often limited to the parts per thousand range.

During studies of inhibition in atomic absorption here, it has been found that the most significant parameters are anion-to-metal mole ratio and flame temperature. This has resulted in the introduction of atomic absorption inhibition titration and its application to silicate[8] and sulfate[9] determinations. The method involves titration of the anion solution with a metal cation solution while the atomic absorption signal for the metal is monitored.

Magnesium was selected as the monitor metal because of its sensitivity for measurement and the high extent of inhibition by refractory forming anions. The anions selected in this study are ortho-, pyro-, tri-, tetra- and hexaphosphates. Observations were made with both total consumption and pre-mix slot burners. A hydrogen–air flame was used in order to have the relatively low flame temperatures and the flame temperature control which is necessary.

EXPERIMENTAL

Apparatus.

The spectrophotometer and essential apparatus for semi-automatic titration have been described[8]. The total consumption burner was a Jarrell-Ash "HETCO" model. The pre-mix burner had a 0.5 × 100 mm slot. For manual titration an ordinary glass buret was used with 0.027-in. I.D. plastic tubing leading into the titration solution in a 250-ml beaker stirred with a magnetic stirrer.

Reagents

All solutions were prepared from reagent-grade material with deionized distilled water (unless specified otherwise). Sodium hexametaphosphate and tetra-

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phosphoric acid were commercial materials (Benlo Chemical Co.). To remove cations, the solution was treated with cation-exchange resin (Dowex 50-X8, 20–25 mesh) in a separatory funnel by a batch method; the cation-exchange resin was treated with dilute acid solution between uses.

Several detergent product brands were selected randomly from among those sold locally.

Titration procedure

Before a titration was begun, gas flow-rates, etc., were adjusted for maximum inhibition with a solution containing magnesium and phosphate. The atomic absorption signal was observed at intervals during the titration by dipping the aspirator tube into the titration vessel. Steps were taken to insure that the titration solution level with reference to the burner did not change and that solution uptake rates did not change sufficiently to introduce significant errors. A complete manual titration curve was obtained in less than 30 min. Semi-automatic titration required less than 5 min.

RESULTS AND DISCUSSION

Total-consumption burner

For the total-consumption burner, the inhibitions by the three anions, orthophosphate, silicate, and sulfate were similar. The extent of inhibition was proportional to the magnesium absorption signal and generally followed the temperature profile of the flame[10]. Rather wide variation of hydrogen-to-air flow-ratios (0.5–4.0) and total gas flow-rates (15–50 $ft^3\ h^{-1}$) showed little effect on the relative amounts of inhibition among the three anions. The degree of inhibition was similar for phosphate and silicate and was somewhat less for sulfate.

The inhibition effect was relatively linear with anion concentration for mole ratios of inhibitor (anion) to absorber (magnesium) less than unity and anion concentrations down to 0.5 $\mu g\ ml^{-1}$. This linear response suggests the possibility of relatively precise and sensitive indirect measurement of these anions by their inhibiting effect (*e.g.*, ref. 4). The selective determination of one anion in the presence of the others is unlikely, however, because the relative inhibitions of sulfate, silicate and phosphate are independent of vertical position, fuel-to-oxidant ratio, total gas flow-rate, and anion concentration.

Pre-mix burner

Results obtained with a pre-mix burner were significantly different from those with the total-consumption burner, because of the smaller range of droplet sizes. With the latter burner, phosphate and silicate inhibited similarly, but with the pre-mix flame, the inhibition changed progressively (Fig. 1). Inhibition for various fuel-to-oxidant flow-rates is also shown in Fig. 1. Several features of these plots are significant. Absorption by magnesium is maximal and inhibitions are at or very near a minimum at hydrogen-to-air flow-ratios of about 0.5; this ratio corresponds to a stoichiometric mixture for combustion of hydrogen with air and thus a maximum in flame temperature. At lower or higher ratios, the cooler flame resulted in more inhibition for all three anions, but also less absorption by magnesium. Observations

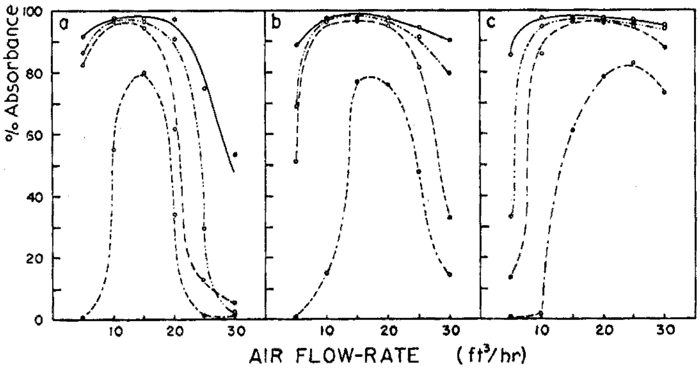

Fig. 1. Inhibition and gas flow-rates. H_2 flow-rates: (a) 5 ft^3 h^{-1}; (b) 10 ft^3 h^{-1}; (c) 15 ft^3 h^{-1}. (——) 5 p.p.m. Mg; (–··–) 5 p.p.m. Mg+20 p.p.m. SO_4; (––––) 5 p.p.m. Mg+20 p.p.m. PO_4; (–·–·) 5 p.p.m. Mg+20 p.p.m. SiO_3. Pre-mix burner. Burner height, 10 mm; $\lambda = 285.2$ nm; pH 7.

for many more combinations of gas flow-rates all yielded a similar pattern. When total gas flow-rate was increased while a constant hydrogen-to-air flow-ratio was maintained, the inhibition decreased because of the increased thermal input to the flame.

Inhibition for all three anions increased moderately with pH and with decreasing height of the beam in the flame. These trends were not distinctive for any one of the anions and were not considered suitable for application to selective determinations of anions.

Data obtained here, in agreement with those of other workers[11], showed that when the mole ratio of inhibiting anion to metal exceeded approximately unity, the extent of inhibition no longer increased as the concentration of anion was increased. At anion–magnesium mole ratios less than unity, discontinuities in solution stoichiometry *vs.* absorption were observed for phosphate and silicate solutions. Titration permitted convenient variation of the solution stoichiometry, and allowed easy maintenance of other experimental conditions during measurements. An example of a curve obtained when phosphate was titrated with magnesium is shown in Fig. 2. The remarkable shape of this curve forms the basis of the new measurement technique for low concentrations of phosphate. It represents a unique type of titration chemistry in that high-temperature processes on small portions of solution are the observed phenomena. Reverse titrations of metals with inhibiting anions might also be advantageous in certain cases.

Phosphate titration

On the titration curve shown in Fig. 2, points suitable for application to phosphate determinations are designated as *a*, *b* and *c*; Table I summarizes mole ratios *vs.* p.p.m. phosphate for each of these end-points. The shape of the curve in Fig. 2 combined with the data of Table I indicates that any of these points may be used for convenient end-point designation. The three titration end-points suggest the formation of refractory compounds with approximately two, three and four magnesium atoms per phosphorus atom. Such stoichiometries do not correspond to magnesium phosphate compounds or complexes of ordinary solution chemistry,

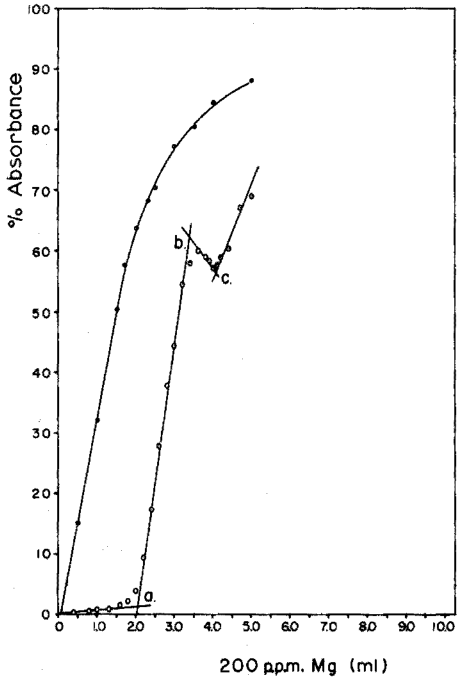

Fig. 2. Titration of blank and 8 p.p.m. orthophosphate. Titrant, $MgCl_2$ solution. Gas flow-rates: 25 $ft^3\ h^{-1}$ H_2 (60 p.s.i.) and 5 $ft^3\ h^{-1}$ air (80 p.s.i.).

TABLE I

MOLE RATIOS OF PHOSPHATE-TO-MAGNESIUM AT THE SUCCESSIVE END-POINTS ON THE TITRATION CURVES

p.p.m. PO_4	*a*	*b*	*c*
20	0.513	—	—
15	0.567	—	—
10	0.556	—	—
8	0.559	0.322	0.269
7	—	0.358	0.319
6	0.515	0.322	0.262
5	0.551	0.319	0.261
4	0.532	0.332	0.283
		0.328	0.291
2	0.609	0.324	0.278
1	0.914	0.360	0.263
0.9	—	0.449	0.231
0.7	—	0.448	0.275
0.5	—	1.49	0.279
0.3	—	0.556	0.209
0.1	—	0.512	0.145
	$\bar{x}=0.542$[a]	0.332[a]	0.268[a]

[a] Means computed for values above line.

but rather reflect high-temperature processes occurring in the evaporating droplets.

The sample droplet is subject to drastic reactions including formation, dehydration and volatilization of dry aerosol particles. All these processes occur in about 1 ms[11,12]. Stoichiometries quite different from those of ordinary solution chemistry are to be expected. The decreasing signal before point *c* can be assigned to a rate process involving formation of a more stable refractory species from a less stable initial species. The effect is even more prominent for solutions containing another anion, as shown in Fig. 3. This titration method allows investigation into the mechanisms, and such studies are presently being pursued in this laboratory.

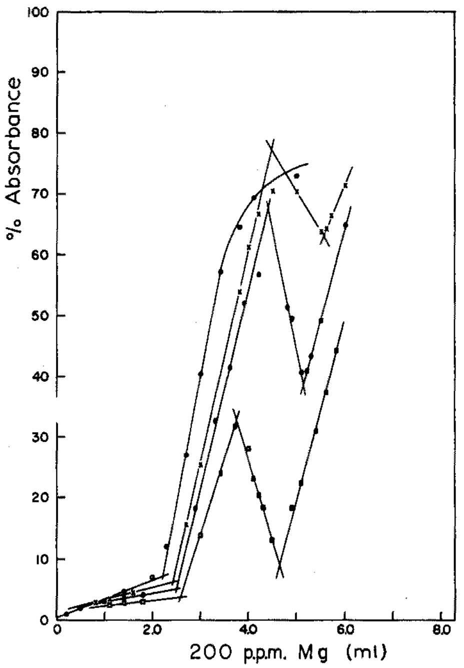

Fig. 3. Titrations. (○) 10 p.p.m. PO_4; (×) 10 p.p.m. $PO_4 + 5$ p.p.m. SO_4; (●) 10 p.p.m. $PO_4 + 10$ p.p.m. SO_4; (□) 10 p.p.m. $PO_4 + 15$ p.p.m. SO_4. Gas flow-rates: as Fig. 2.

TABLE II

MOLE RATIOS OF PHOSPHATE-TO-MAGNESIUM AT THE END-POINTS FOR SOLUTIONS CONTAINING PHOSPHATE AND SULFATE

p.p.m. PO_4	*p.p.m.* SO_4	*a*	*b*	*c*
5	10	0.613	0.376	0.285
10	0	0.556		
10	5	0.527	0.297	0.244
10	10	0.551	0.321	0.263
10	15	0.538	0.366	0.289
15	10	0.602	0.334	0.248
		$\bar{x}=0.564$	0.339	0.262

Table II summarizes results for titrations of solutions containing sulfate as well as phosphate. The data show general agreement with titrations where no sulfate was present. The effects of sulfate on the titration curve were to decrease the absorption throughout the titration and to enhance the minimum at point *c*.

Polyphosphate titrations

Polyphosphate titration curves had the same general shapes as those for orthophosphate. Titration stoichiometry was examined under the same instrumental settings as for phosphate titration. The end-points used corresponded to point *a* of Fig. 2. The magnesium-to-phosphorus ratio approached a constant value of unity with increasing size of the polyphosphate (Fig. 4), whereas for orthophosphate the ratio was near two. These results suggest a kinetically determined inhibiting process in the droplets.

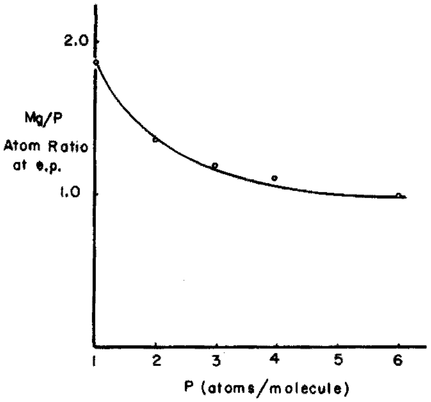

Fig. 4. Variation of end-point stoichiometry with size of polyphosphates.

Silicate can be expected to interfere when present in samples. It must be either separated, or determined by a different inhibition titration[8] and subtracted from the total silicate and phosphate results as obtained here.

Determinations in practical samples

Analysis of Milwaukee river water was performed in order to examine the utility of the system. The slightly acidified sample was filtered through paper and then through a 0.4-μm membrane filter. It was then passed through a cation-exchange column in the acid form to replace naturally occurring magnesium, calcium and other cations. The sample was diluted ten-fold for convenience. Titrations were performed on river water, river water plus standard addition of phosphate, and standardized phosphate solutions. The results are shown in Table III. Accuracy and precision are good considering the speed and sensitivity of the method. The absence of measurable silicates in the samples titrated was confirmed by observing a negligible end-point for a titration in conditions under which only silicate would be detected[8]. Thus, either the river water contained negligible dissolved silicate or silicate was quantitatively held in the cation exchanger. Complete ion exchange of naturally occurring magnesium was indicated by virtually zero absorbance at the beginning of the titration. Other interfering cations were apparently also completely and conveniently exchanged. Results were similar whether the standard addition of phosphate was made before or after passing the sample through the ion-exchange column. Thus, recovery of phosphate from the ion-exchange column was apparently complete.

Examination of the first column on Table III indicates that the end-point stoichiometry can vary somewhat for separate flame adjustments. For best results, therefore, a standard or a standard addition must be titrated with the same flame adjustment and instrument settings used for the samples.

TABLE III

ANALYSIS OF RIVER WATER

End-point (ml)			*Concentration (p.p.m.)*	
2 p.p.m. PO_4	*River*	*River + 2 p.p.m. PO_4*	*PO_4 in river water*	*Added PO_4 determined*
0.73	1.50	2.24	4.14	1.97
0.59	1.23	1.80	4.10	1.93
0.50	1.08	1.60	4.40	2.08
0.51	1.05	1.61	4.32	2.16
0.57	1.29	1.84	4.46	2.12
			$\bar{x}=4.28$	$\bar{x}=2.05$
			$s=0.16$	$s=0.10$

TABLE IV

DETERMINATION OF PHOSPHATE IN DETERGENTS

Brand #	*PO_4 found (%)*	
	Inhibition titration[a]	*Standard method*[b]
1	36.2±0.5	35.8
2	36.1±0.2	36.5
3	36.1±0.5	36.6
4	28.9±1.0	24.6

[a] Standard deviations based on five replicate titrations. Percent PO_4 in commercial material as received.
[b] Ref. 13.

Phosphate was also determined in four brands of commercial detergent products (Table IV). The detergent solutions were either boiled for 1 h or aged for several days before titration.

Sample No. 1 of the series of water analysis standard solutions offered by the Federal Water Quality Control Administration, was analyzed. The result obtained was 0.050 ($s=0.001$) p.p.m. phosphorus, compared with the stated value by FWDA of 0.05 p.p.m.

Conclusion

The results of this investigation indicate that atomic absorption inhibition titration is applicable to the determination of phosphate in surface and waste waters. A pre-mix burner was necessary.

When the phosphate solution was titrated with magnesium, three break points were found. At these points the magnesium-to-phosphate ratio remained essentially constant, and the points could therefore serve as the end-points for titration, even in the presence of sulfate.

The polyphosphate results suggest a kinetically determined inhibition process in the droplets. Applications to various types of phosphate solutions in water yielded suitable accuracy and precision.

Financial support was provided by the Federal Water Quality Administration, Environmental Protection Agency, Grant No. 16020 DHD. Polyphosphate samples were donated by the Benlo Chemical Co., Milwaukee, Wisc.

SUMMARY

The atomic absorption inhibition titration of phosphates was studied for two types of burner. Dependence on gas flow-rates was observed. The method with a pre-mix burner was employed to determine phosphate in surface and waste waters. The results are compared with those by the standard method. The proposed method was found to be rapid, simple and accurate.

RÉSUMÉ

On propose une méthode par absorption atomique pour le dosage des phosphates, en utilisant deux types de bruleurs. Ce procédé a été employé pour des analyses d'eaux de surface et d'eaux résiduaires. Il présente les avantages d'être rapide, simple et précis.

ZUSAMMENFASSUNG

Die Atomabsorptionsinhibitionstitration von Phosphat wurde unter Anwendung zweier Brennerarten untersucht. Es wurde eine Abhängigkeit von den Gas-Strömungsgeschwindigkeiten beobachtet. Die Methode, bei der ein Laminarbrenner eingesetzt wird, wurde auf die Bestimmung von Phosphat in Oberflächenwasser und Abwasser angewendet. Die Ergebnisse werden mit denen der Standardmethode verglichen. Die vorgeschlagene Methode ist schnell, einfach und genau.

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Analytica Chimica Acta, 64 (1973) 397–408

TITRAGE POTENTIOMETRIQUE DES THIOLS EN MILIEU ORGANIQUE A L'AIDE D'UNE ELECTRODE A MONOCRISTAL DE SULFURE D'ARGENT

COMPARAISON AVEC UNE ELECTRODE ARGENT–SULFURE D'ARGENT CLASSIQUE

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Le dosage des thiols (mercaptans) est un problème analytique fréquent dans l'industrie, pétrolière et pharmaceutique notamment. De nombreuses méthodes ont été proposées, tant pour les thiols solubles dans l'eau que pour ceux solubles uniquement en milieu organique.

Elles sont exposées dans divers ouvrages généraux[1–4] et ont fait l'objet en 1962, d'une mise au point de Pellerin[5]. Parmi elles, on trouve plusieurs méthodes électrochimiques, méthodes qui ont été particulièrement utilisées en milieu organique. Nous citerons la coulométrie[6], la polarographie classique[7,8], la polarographie oscillographique[9], la polarographie à tension carrée[10,11], l'ampérométrie[12–18] et la potentiométrie[19–30].

Les titrages potentiométriques, par leur simplicité de mise en oeuvre et leur semi-automatisation facile, se prêtant bien aux analyses en série, présentent un intérêt particulier. En général, on opère par précipitation des thiolates d'argent. Aux thiols en solution soit dans l'eau, soit dans les mélanges du type éthanol–benzène, on ajoute une solution aqueuse ou alcoolique de nitrate d'argent. On suit la réaction en mesurant le potentiel d'une électrode d'argent plongée dans le milieu réactionnel. Si l'on veut obtenir des mesures exactes et reproductibles, ainsi que des sauts de potentiel importants au point équivalent de la réaction de précipitation, il est nécessaire de traiter cette électrode préalablement à chaque titrage. Plusieurs prétraitements sont possibles, l'un des plus couramment utilisé consistant en la sulfuration de l'électrode d'argent, soit par voie chimique, soit par voie électrochimique. Dans le cas du prétraitement chimique, on immerge l'électrode d'argent, préalablement décapée et polie, dans une solution aqueuse d'un sulfure alcalin à laquelle on ajoute lentement et sous agitation énergique, du nitrate d'argent. Le prétraitement électrochimique consiste en une oxydation anodique de l'argent de l'électrode en Ag(I) au sein d'une solution d'ions sulfure. Dans l'un et l'autre cas, il se dépose sur l'électrode d'argent une fine pellicule adhérente de sulfure d'argent. Ces traitements sont délicats et doivent être recommencés fréquemment, ce qui est gênant en analyse de routine.

L'apparition d'électrodes à membrane dites "spécifiques", et en particulier d'une électrode indicatrice des ions sulfure d'un emploi commode, nous a donc incités à étudier ses possibilités pour suivre le titrage des thiols par potentiométrie à courant nul.

PARTIE THÉORIQUE

L'électrode indicatrice des ions sulfure a déjà fait l'objet de nombreuses études en solution aqueuse[29, 31–36]. Rappelons qu'elle est constituée d'un mince monocristal synthétique de sulfure d'argent (épaisseur 2 mm environ) dont l'une des faces (dite face externe) est baignée par la solution étudiée tandis que la face interne est baignée par une solution aqueuse de nitrate d'argent dans laquelle plonge une électrode de référence constituée par un simple fil d'argent (l'activité des ions Ag^+ dans cette solution étant constante, le potentiel du fil d'argent est, lui aussi, constant).

Lorsque cette électrode est plongée dans une solution d'ions Ag^+ il se développe de part et d'autre de la membrane monocristalline un potentiel donné par la loi de Nernst:

$$E = E_0 + 0.058 \log [Ag^+] \text{ à } 20°$$

$[Ag^+]$ représentant l'activité des ions argent dans la solution considérée.

Si maintenant l'électrode est plongée dans une solution ne contenant pas d'ions Ag^+ mais des ions sulfure S^{2-}, une certaine quantité (infime) du monocristal va passer en solution selon:

$$Ag_2S\downarrow \rightleftharpoons 2\,Ag^+ + S^{2-}$$

jusqu'à ce que les activités de Ag^+ et S^{2-} vérifient la relation du produit de solubilité de Ag_2S:

$$[Ag^+]^2[S^{2-}] = s$$

et le potentiel de l'électrode est donné par:

$$E = E_0' - 0.029 \log [S^{2-}]$$

avec:

$$E_0' = E_0 - 0.29 \text{ p}s \qquad (\text{p}s = -\log s)$$

Le potentiel de l'électrode est ainsi fonction de l'activité des ions sulfure dans la solution.

Un raisonnement identique peut être fait avec tout anion donnant un sel d'argent insoluble ce qui est le cas des ions thiolate $R–S^-$. Soit s' le produit de solubilité d'un thiolate d'argent:

$$[Ag^+][R–S^-] = s'$$

Le potentiel de l'électrode plongeant dans une solution de RS^- sera donné par:

$$E = E_0'' - 0.058 \log [RS^-]$$

On peut, dès lors, suivre au moyen de l'électrode des réactions chimiques variées mettant en jeu S^{2-} ou RS^-, en particulier la précipitation du sulfure et d'un thiolate d'argent.

Dans le cas de la précipitation du sulfure d'argent:

$$2\,Ag^+ + S^{2-} \rightarrow Ag_2S\downarrow$$

si l'on opère en milieu de force ionique constante, le potentiel de l'électrode est donné par l'équation:

$$E = E_1 + 0.058 \log [Ag^+] \tag{1}$$

$[Ag^+]$ étant la concentration des ions argent dans la solution, E_1 étant différent de E_0, potentiel normal à dilution infinie.

Désignons par V le volume d'électrolyte utilisé, c' et v' la concentration et le volume de la prise d'essai de sulfure, c et v la concentration et le volume de la solution de nitrate d'argent ajoutée, le bilan matière s'écrit:

$$\frac{c\,v}{V+v+v'} = [Ag^+] + 2\left(\frac{c'\,v'}{V+v+v'} - [S^{2-}]\right)$$

Si l'on tient compte de la relation du produit de solubilité du sulfure d'argent, cette équation devient:

$$[Ag^+]^3 + [Ag^+]^2\left(\frac{2\,c'\,v'}{V+v+v'} - \frac{c\,v}{V+v+v'}\right) - 2s = 0 \tag{2}$$

On peut alors aisément, à l'aide d'une calculatrice électronique, calculer à tout moment la concentration $[Ag^+]$ en fonction des grandeurs expérimentales et ainsi tracer la courbe théorique de variation du potentiel de l'électrode au cours du titrage.

De même dans le cas de la précipitation d'un thiolate d'argent:

$$Ag^+ + RS^- \rightarrow AgRS\downarrow$$

Si c'' et v'' représentent respectivement la concentration et le volume de la solution de thiol utilisée, le potentiel théorique de l'électrode indicatrice sera donné par les deux équations suivantes:

$$E = E_1 + 0.058 \log [Ag^+]$$

$$[Ag^+]^2 + [Ag^+]\left(\frac{c''\,v'' - c\,v}{V+v+v''}\right) - s' = 0 \tag{3}$$

Les raisonnements précédents s'appliquent en principe d'une manière identique à l'électrode classique argent–sulfure d'argent.

Nous nous sommes donc proposés d'une part de vérifier si les prévisions théoriques précédentes étaient vérifiées dans le cas de la précipitation des thiolates d'argent en milieu organique, d'autre part de comparer l'électrode à monocristal de sulfure d'argent à l'électrode argent–sulfure d'argent.

PARTIE EXPÉRIMENTALE

Produits chimiques et solutions

Le solvant utilisé pour effectuer les titrages est un mélange éthanol–benzène 2:1 en volume, tamponné en milieu basique par le mélange ammoniaque–nitrate d'ammonium à la concentration $4 \cdot 10^{-2}\ M$.

Les solutions-mères des thiols sont préparées par dissolution du produit pur (Fluka, purum) dans l'isooctane: le thiol est prélevé dans une mince ampoule de verre préalablement tarée qui est aussitôt scellée, pesée puis brisée au sein du solvant. Les solutions ainsi préparées sont conservées au réfrigérateur. La solution de sulfure d'hydrogène dans l'isooctane a été préparée par barbotage du gaz dans le solvant; elle est conservée dans la partie la plus froide du réfrigérateur. Les concentrations de ces solutions étaient de l'ordre de $5 \cdot 10^{-2}$ M. Leurs titres respectifs ont été déterminés préalablement à chaque série de mesure sur l'électrode à monocristal par titrage par une solution de nitrate d'argent, le point équivalent étant repéré par potentiométrie à une électrode argent–sulfure d'argent selon la méthode de Tamele *et al.*[21]. Le titre des solutions de thiols varie très peu sur plusieurs semaines lorsque la solution est conservée à l'obscurité au réfrigérateur. Au contraire le titre de la solution de sulfure d'hydrogène varie dans les mêmes conditions de 5 à 10% par jour.

La solution alcoolique de nitrate d'argent 10^{-2} M a été préparée par dilution d'une solution aqueuse 0.1 M (Titrisol, Merck) dans de l'isopropanol traité par la méthode de Tamele et Ryland[19] puis distillé. Rappelons que ce traitement a pour but l'élimination des traces d'aldéhydes qui altèrent le titre des solutions de nitrate d'argent en réduisant l'argent(I) en argent métallique. Le titre de la solution de nitrate d'argent est déterminé par titrage par une solution d'acide chlorhydrique 0.1 M et potentiométrie à une électrode d'argent.

L'éthanol, l'isopropanol et l'isooctane étaient des produits Prolabo, qualité R.P. Tous les autres produits chimiques (à l'exception des thiols) étaient d'origine Merck, pro analysis.

Electrodes et appareils de mesure

L'électrode indicatrice des ions sulfure était de marque Orion, modèle 94-16A. L'électrode argent–sulfure d'argent a été préparée indifféremment par voie chimique ou électrochimique, les résultats obtenus dans l'un ou l'autre cas étant identiques.

L'électrode de référence du type Ag/AgCl en milieu éthanol–benzène 2:1 a été réalisée selon le modèle préconisé par Popov et Geske[37] dans le cas de l'acétonitrile ou par Cauquis et Serve[38] dans le cas du nitrométhane. Le contact électrique de l'élément de référence avec la solution est assuré par un pont rempli du solvant éthanol–benzène 2:1, ammoniaque–nitrate d'ammonium.

Nous avons vérifié par le tracé des courbes intensité–potentiel sur électrode tournante que le système Ag/Ag$^+$ est un système rapide dans le solvant considéré et que le potentiel de l'électrode de référence est stable plusieurs mois par rapport à celui du système ferrocène–ferricinium. On trouve:

$$E^0_{\mathrm{Ag/AgCl}} - E^0_{\mathrm{Fc/Fc^+}} = -300 \text{ mV}$$

Le pH des solutions a été mesuré au moyen d'une électrode de verre Tacussel pour haute alcalinité type TB/HA (pH-mètre Tacussel type TS 60/N). Nous avons tout d'abord vérifié que le comportement de cette électrode était correct dans le solvant éthanol–benzène (variation de potentiel de 58 mV environ par unité de pH pour des solutions d'acide perchlorique 10^{-1}, 10^{-2} et 10^{-3} M). Si l'on choisit comme origine de l'échelle de pH dans ce milieu pH 1 pour une solution d'acide perchlorique 0.1 M le tampon ammoniaque–nitrate d'ammonium utilisé correspond à un pH parfaitement stable au cours des titrages de 10.8.

Le potentiel de l'électrode Orion et de l'électrode argent sulfure d'argent a été mesuré au moyen d'un millivoltmètre digital Orion type 801.

Cellule et conditions de titrage

Tous les titrages ont été effectués dans une cellule à jaquette thermostatique Metrohm (modèle EA 876/20). La température était régulée à 20° au moyen d'un thermostat à circulation Tamson type T3.

Les sulfures et les thiols considérés sont très facilement oxydables en milieu alcalin. Il est donc impératif d'éliminer très soigneusement l'oxygène dissous du milieu réactionnel par barbotage d'azote pendant 20 min. Nous avons utilisé de l'azote R dont on élimine les traces d'oxygène par passage sur un catalyseur au cuivre (catalyseur BTS, Bayer) et que l'on sature ensuite de vapeurs de solvant par la traversée d'un flacon laveur.

Toutes les additions de solutions dans la cellule de mesure ont été effectuées au moyen de microburettes à piston RGI, le contenu de la cellule étant maintenu en permanence sous courant d'azote exempt d'oxygène.

RÉSULTATS EXPÉRIMÉNTAUX

Réponse des électrodes aux ions argent

Les potentiels pris par l'électrode indicatrice des ions sulfure et par l'électrode argent–sulfure d'argent dans diverses solutions de nitrate d'argent de concentrations connues en milieu éthanol–benzène ont été mesurés. Le potentiel d'équilibre est atteint très rapidement, au plus en une minute. Pour les deux électrodes, la loi de Nernst est suivie dans le domaine de concentration en Ag(I) 10^{-2}–10^{-5} *M* (pente 63.5 mV/unité de pAg pour l'électrode indicatrice des ions sulfure; 61.6 mV/unité de pAg pour l'électrode argent–sulfure d'argent).

Réponse des électrodes aux thiols

La Fig. 1 représente les variations en fonction de la concentration du potentiel

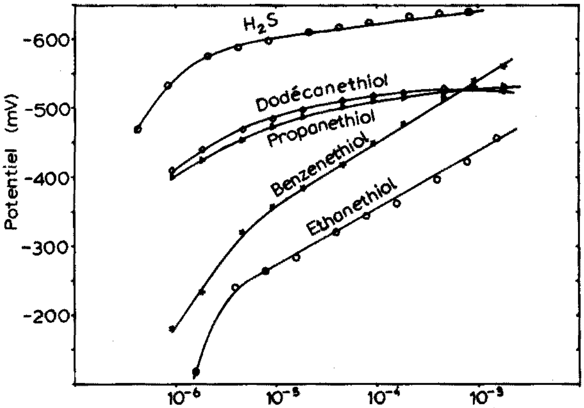


Fig. 1. Variation de $E = f(\log [RSH]_t)$ dans le cas de l'électrode à monocristal de sulfure d'argent.

pris par l'électrode indicatrice des ions sulfure dans diverses solutions de thiols: éthanethiol, propanethiol, dodécanethiol, benzènethiol et dans une solution de sulfure d'hydrogène. Dans le domaine de concentration 10^{-2}–10^{-5} M, certaines réponses sont sensiblement linéaires: éthanethiol (pente 84 mV), benzènethiol (pente 93 mV), sulfure d'hydrogène (pente 26 mV). Mais seule la réponse au sulfure d'hydrogène peut être considérée comme nernstienne (pente théorique 30 mV). Pour les autres thiols considérés, la réponse de l'électrode n'obéit pas à une loi simple.

Dans le cas de l'électrode argent–sulfure d'argent (Fig. 2), on constate également que seules les réponses à l'éthanethiol (pente 63 mV), au benzènethiol (pente 97 mV) et au sulfure d'hydrogène (pente 30 mV) sont linéaires dans le domaine de concentration 10^{-2}–10^{-5} M. Les pentes des droites pour l'éthanethiol et le sulfure d'hydrogène sont voisines des pentes théoriques.

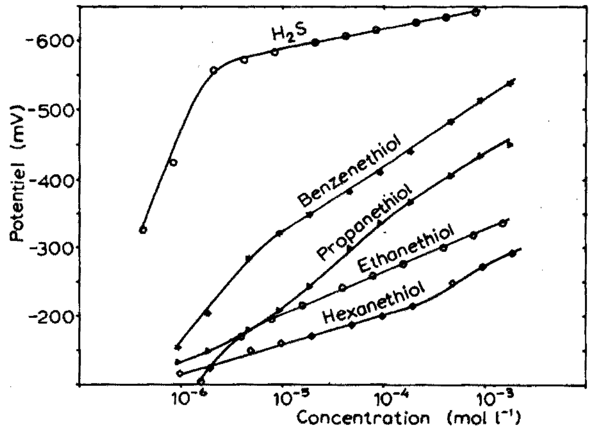
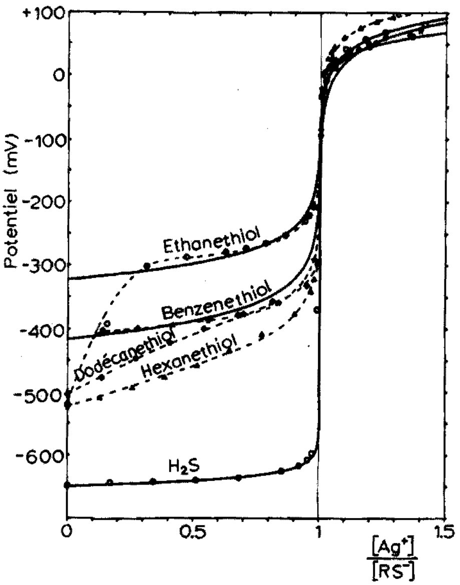


Fig. 2. $E = f(\log [\mathrm{RSH}]_t)$. Electrode argent–sulfure d'argent.

Titrage potentiométrique des thiols avec l'électrode à monocristal de sulfure d'argent

Nous avons suivi la précipitation de différents thiols à des concentrations de l'ordre de 10^{-3} M par le nitrate d'argent, avec l'électrode indicatrice des ions sulfure. Les courbes expérimentales représentées en pointillé (Fig. 3) ont toutes été tracées point par point. Après chaque addition d'argent, le potentiel d'équilibre est atteint en 3 min environ, sauf au voinisage immédiat du point équivalent où 10 min sont nécessaires; dans le cas de l'éthanethiol et du benzènethiol, le potentiel augmente rapidement au début du dosage de −520 mV à environ −300 mV et −400 mV respectivement. Ce potentiel "plateau" étudié par Karchmer[2] pour une électrode argent–sulfure d'argent, est caractéristique de l'électrode utilisée et du thiol dans un solvant donné. Le saut de potentiel au point équivalent dépend aussi du thiol considéré: par exemple, de l'éthanethiol à l'hexanethiol, le saut de potentiel diminue de 150 mV. Il reste cependant, toujours nettement inférieur au saut observé lors du titrage du sulfure d'hydrogène (700 mV). Sur cette même Figure, nous avons tracé en trait plein, la courbe théorique de la variation du potentiel au cours du titrage du sulfure d'hydrogène. Elle a été réalisée sur la table traçante d'une calculatrice Hewlett-Packard 9100 A en programmant les équations

(1) et (2). Les potentiels du début et de la fin du titrage permettent de déduire le produit de solubilité apparent du sulfure d'argent dans le solvant utilisé ($s = 10^{-34.5}$). Il est possible de faire les mêmes calculs pour les titrages de certains thiols lorsque la réponse de l'électrode à ceux-ci, bien que ne suivant pas la loi de Nernst, est linéaire. C'est le cas pour l'éthanethiol et pour le benzènethiol. On programme alors les équations (1) et (3), dans lesquelles la pente théorique de 58 mV est remplacée par les valeurs des pentes expérimentales, respectivement 84 et 93 mV. Avec cette réserve, on peut en déduire les produits de solubilité apparents de l'éthanethiolate ($s = 10^{-11.6}$) et du benzènethiolate d'argent ($s = 10^{-12.5}$).



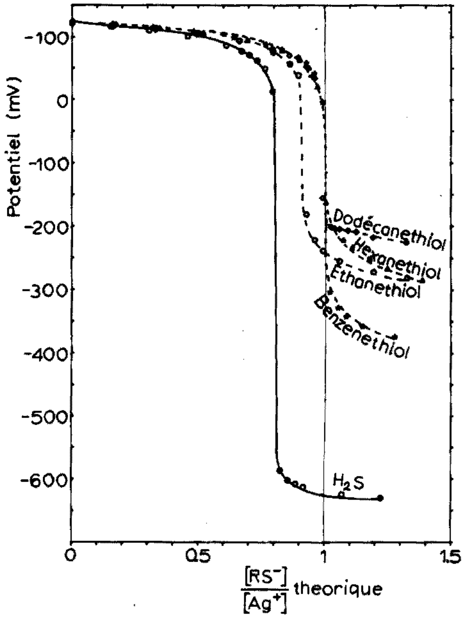


Fig. 3. Titrage potentiométrique de quelques thiols par l'argent. Electrode à monocristal de sulfure d'argent. (——) Courbes du potentiel théorique, (-----) courbes expérimentales.

Fig. 4. Titrage potentiométrique de Ag^+ par H_2S et par quelques thiols. Electrode à monocristal de sulfure d'argent.

Si l'on effectue le titrage en sens inverse (Fig. 4), c'est-à-dire la précipitation de l'argent par le thiol, la hauteur du saut de potentiel reste identique dans le cas du benzènethiol, de l'éthanethiol et du sulfure d'hydrogène. Elle devient moins importante pour l'hexanethiol et le dodécanethiol. Par ailleurs, avec cet ordre d'addition des réactifs, les points équivalents observés dans le cas du sulfure d'hydrogène et de l'éthanethiol diffèrent notablement des points équivalents théoriques correspondants (de 20 et 10% respectivement). Ce phénomène, parfaitement reproductible, sera explicité plus longuement dans un mémoire ultérieur. Du point de vue de l'analyste, en effet, c'est le dosage des thiols par addition d'une solution titrée d'ions Ag^+ qui est important et non l'inverse.

Comparaison de l'électrode à monocristal de sulfure d'argent et de l'électrode argent–sulfure d'argent

Nous avons représenté (Fig. 5) les courbes obtenues lors de la précipitation de quelques thiols par le nitrate d'argent, dans le cas de l'électrode à monocristal et dans celui de l'électrode argent–sulfure d'argent. Si pour l'éthanethiol, l'écart entre les potentiels est pratiquement nul sauf au début du titrage, pour le butanethiol et l'hexanethiol, l'écart entre les potentiels est très important. Le saut de potentiel est nettement plus grand pour les mesures effectuées à l'aide de l'électrode à monocristal. Quand au comportement du benzènethiol, il est identique à celui de l'éthanethiol et ceux du propanethiol et du dodécanethiol se rapprochent de celui de l'hexanethiol.

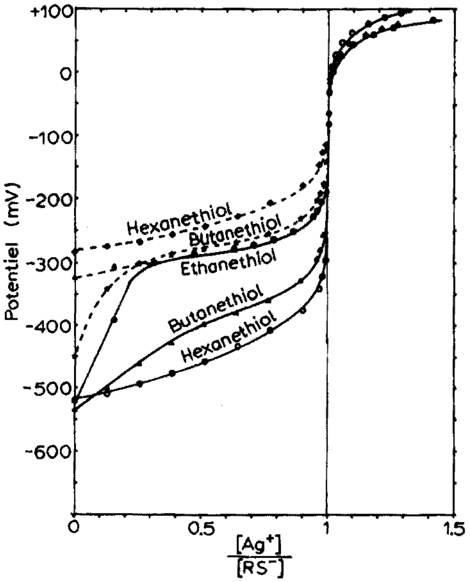
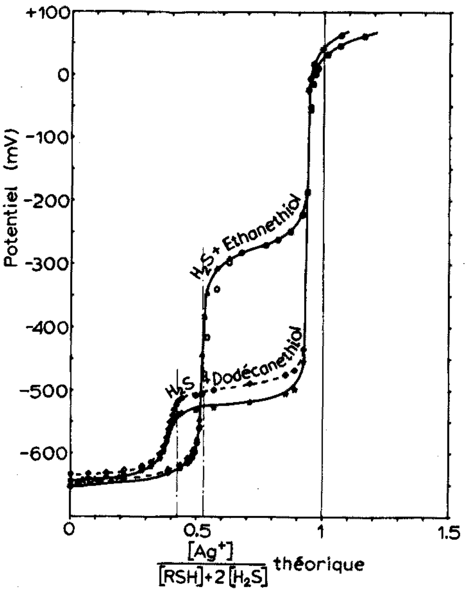


Fig. 5. Comparaison du titrage potentiométrique de différents thiols par l'argent avec l'électrode à monocristal (——) et l'électrode classique argent–sulfure d'argent (– – – – –).

D'une point de vue purement pratique, cette différence est avantageuse dans le cas du titrage des thiols à chaine longue.

Dosage des mélanges H_2S–thiols

Nous avons comparé le comportement des deux types d'électrode dans le cas des mélanges H_2S–éthanethiol et H_2S–dodécanéthiol. D'après ce qui précède, le comportement devrait être identique pour les deux électrodes avec le premier mélange et différent avec le second. La vitesse de réponse des électrodes jouant un rôle important dans ces exemples, nous avons été amenés à opérer avec des intervalles de temps entre les mesures plus ou moins longs. La Fig. 6 représente les courbes de titrage lorsque l'on attend 1 min entre chaque addition d'argent. La Fig. 7 représente les mêmes courbes lorsque l'on attend 3 min.



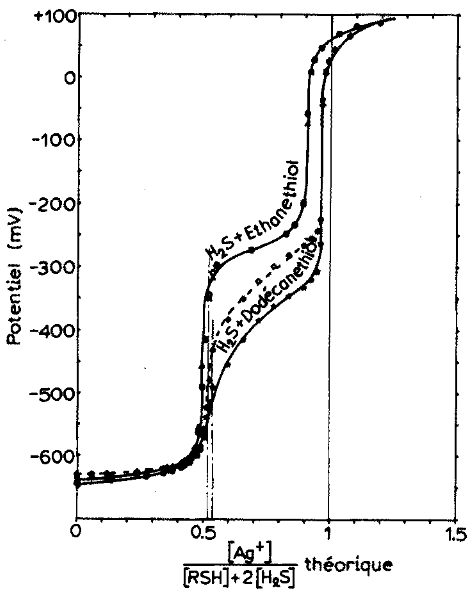


Fig. 6. Titrage de mélanges H_2S–thiols par l'argent. Le potentiel est lu une minute après chaque addition d'argent. (——) Electrode à membrane de sulfure d'argent, (-----) électrode argent–sulfure d'argent, (–·–·) points équivalents théoriques.

Fig. 7. Titrage de mélanges H_2S–thiols par l'argent. Le potentiel est lu trois minutes après chaque addition d'argent. (——) Electrode à membrane de sulfure d'argent, (----) électrode argent–sulfure d'argent, (–·–·) points équivalents théoriques.

Pour les mélanges H_2S–éthanethiol, les courbes tracées avec l'électrode à monocristal ou avec l'électrode argent–sulfure d'argent sont identiques. Le temps d'attente n'a aucune influence sur les deux sauts de potentiels observés. En revanche, un temps plus long altère l'exactitude du dosage. En effet, si le point équivalent correspondant à H_2S (1er saut de potentiel) coïncide bien avec le point équivalent théorique, celui qui correspond à l'éthanethiol diffère notablement du point équivalent théorique et l'écart augmente avec le temps d'attente (5% pour 1 min d'attente, 10% pour 3 min).

Pour les mélanges H_2S–dodécanethiol, les courbes tracées avec chacune des deux électrodes sont différentes. Le saut de potentiel correspondant à H_2S est plus important pour l'électrode argent–sulfure d'argent que pour l'électrode à monocristal. De plus, le temps d'attente influe notablement sur ce saut. Celui-ci est pratiquement doublé d'une minute d'attente à trois minutes d'attente. En revanche, ce temps ne modifie pas l'écart avec le point équivalent théorique pour le saut de potentiel correspondant au dodécanethiol, écart qui est de 4% environ dans les deux cas.

La semi-automatisation des titrages potentiométriques des mélanges H_2S–thiols est aisée et nous l'avons réalisée dans le cas des deux électrodes indicatrices à l'aide d'un potentiographe Metrohm (E 336A) à burette automatique. La vitesse de réponse des électrodes est suffisante pour permettre un titrage en continu. Les résultats ainsi obtenus confirment les courbes précédentes, tracées point par point.

CONCLUSIONS

L'électrode à monocristal de sulfure d'argent, dite spécifique des ions sulfure présente en milieu éthanol–benzène, une réponse non nernstienne pour les différents thiols considérés. Il en est de même pour l'électrode argent–sulfure d'argent classique. Ces deux électrodes ne peuvent donc être utilisées avec sécurité pour le dosage des thiols par simple mesure du potentiel.

En revanche le titrage des thiols par précipitation des thiolates d'argent correspondants peut être parfaitement suivi avec l'électrode à monocristal de sulfure d'argent. Les sauts de potentiel au point équivalent sont plus importants qu'avec l'électrode argent–sulfure d'argent classique et ce d'autant plus que la chaîne du thiol est plus longue. D'autre part la simplicité d'emploi de l'électrode à monocristal est un avantage important dans la pratique: pas de préparation de l'électrode ni de renouvellement périodique de la couche de sulfure d'argent c'est-à-dire aucun entretien de l'électrode.

En ce qui concerne les mélanges H_2S–thiols, on observe des erreurs systématiques par défaut dans le dosage du thiol, dues probablement à des phénomènes de co-précipitation du sulfure d'argent et du thiolate d'argent et d'adsorption du thiol sur le précipité de sulfure d'argent. Par ailleurs, la forme des courbes dépend beaucoup de la vitesse d'addition du réactif.

L'électrode à monocristal de sulfure d'argent apparaît ainsi comme un moyen commode pour suivre la précipitation des thiolates d'argent par potentiométrie à courant nul.

RÉSUMÉ

Les réponses de l'électrode à membrane de sulfure d'argent, dite "spécifique des ions sulfure", à différents thiols primaires et aromatiques et au sulfure d'hydrogène ont été étudiées en milieu éthanol–benzène; elles ne sont généralement pas nernstiennes. Cette électrode peut cependant être parfaitement utilisée pour suivre par potentiométrie à courant nul, la précipitation des thiols et des mélanges thiols–sulfure d'hydrogène par les ions argent. Les sauts de potentiel observés sont comparables à ceux obtenus avec une électrode argent–sulfure d'argent classique. Ne nécessitant aucun prétraitement ni aucun entretien, l'électrode à membrane de sulfure d'argent apparaît ainsi comme très commode pour le dosage des sulfures et des thiols dans les produits pétroliers.

SUMMARY

The responses of the silver sulfide membrane electrode (the so-called sulfide-selective membrane electrode) to different primary and aromatic thiols and to hydrogen sulfide have been studied in an ethanol–benzene mixture. They have not been found in good agreement with the Nernst relationship. However, this electrode can readily be used to follow, by potentiometry, the precipitation of thiols and thiol–hydrogen sulfide mixtures with silver ions. The observed potential breaks are similar to those obtained with a conventional silver–silver sulfide electrode. As it needs neither pretreatment nor maintenance, the silver sulfide membrane electrode is therefore suitable for determining hydrogen sulfide and thiols in petroleum products by potentiometric titration.

ZUSAMMENFASSUNG

Das Verhalten der Silbersulfid-Membranelektrode (der sog. sulfidselektiven Membranelektrode) gegenüber verschiedenen primären und aromatischen Thiolen und Schwefelwasserstoff in äthanolisch–benzolischen Lösungen wurde untersucht. Die Übereinstimmung mit der Nernstschen Beziehung war nicht gut. Jedoch kann diese Elektrode ohne weiteres dazu verwendet werden, die Fällung von Thiolen und von Thiol–Schwefelwasserstoff-Gemischen mit Silberionen potentiometrisch zu verfolgen. Die beobachteten Potentialsprünge sind ähnlich denen, die mit einer herkömmlichen Silber–Silbersulfidelektrode erhalten werden. Da Vorbehandlung und Unterhaltung nicht notwendig sind, eignet sich die Silbersulfid-Membranelektrode für die Bestimmung von Schwefelwasserstoff und Thiolen in Erdölprodukten durch potentiometrische Titration.

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POTENTIOMETRIC STUDIES ON THIOACETAMIDE BY MEANS OF A SULPHIDE ION-SELECTIVE MEMBRANE ELECTRODE

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Thioacetamide is a well known reagent which is used in both qualitative and quantitative analysis[1,2].

In the present report, a rapid and accurate potentiometric method is described for the determination of thioacetamide with a sulphide ion-selective membrane electrode. The products of the reaction with silver nitrate titrant have been identified.

EXPERIMENTAL

E.m.f. measurements were taken with a Radelkis Precision pH meter Type OP-205 (Radelkis, Budapest, Hungary). A Radelkis sulphide ion-selective electrode Type OP-S-711 and a Metrohm pH glass electrode were used as indicator electrodes and a saturated calomel electrode as reference electrode. The calomel electrode was connected with the solution to be titrated by a 1 *M* potassium nitrate–agar salt bridge.

Ultraviolet and visible spectra were recorded by a Unicam SP 700 spectrophotometer, and the infrared spectra by a Zeiss UR-10 instrument.

All reagents used were of analytical grade.

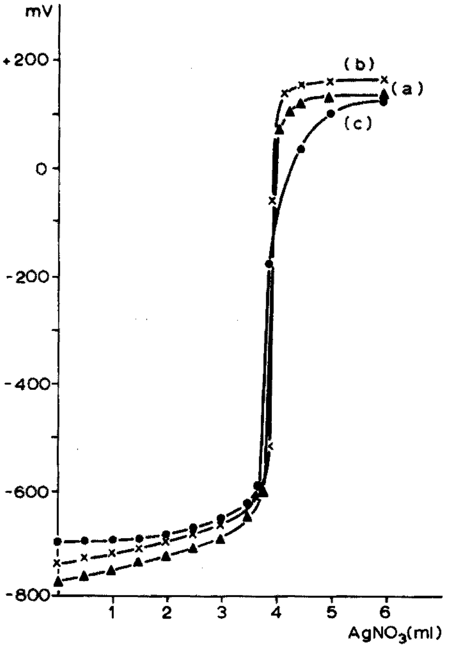
A thioacetamide stock solution (10^{-1} *M*) was prepared by weighing and dissolving the appropriate amount of the reagent.

Dilute standard solutions were prepared from the stock solution by serial dilution.

RESULTS

The potentiometric titration curves of 10^{-1}–10^{-3} *M* thioacetamide solutions were established in 1 *M* sodium hydroxide (Fig. 1), in 0.1 *M* sodium hydroxide (Fig. 2), in 0.01 *M* ammonia solution (Fig. 3), in pure distilled water (Fig. 4), and in 0.1 *M* acetic acid (Fig. 9). Silver nitrate solution of the equivalent concentration was used as titrant in every case.

In Figs. 5 and 6, the potential and pH change are shown for the titration of thioacetamide of the same concentration, in 0.01–0.05 *M* and 0.1 *M* sodium hydroxide. In Figs. 7 and 8 are presented the changes in the course of the titration of thioacetamide in 0.01–0.1 *M* ammonia solution.



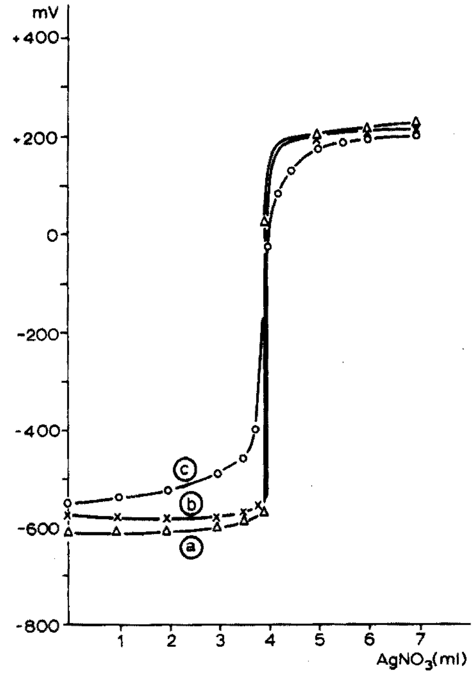


Fig. 1. Potentiometric titration curves of thioacetamide in 1 M sodium hydroxide. (a) 10^{-1} M thioacetamide; (b) 10^{-2} M thioacetamide; (c) 10^{-3} M thioacetamide.

Fig. 2. Potentiometric titration curves of thioacetamide in 10^{-1} M sodium hydroxide. (a, b, c) As in Fig. 1.

In Fig. 10 are shown the titration curves obtained in the presence of 0.1 M and 0.5 M nitric acid.

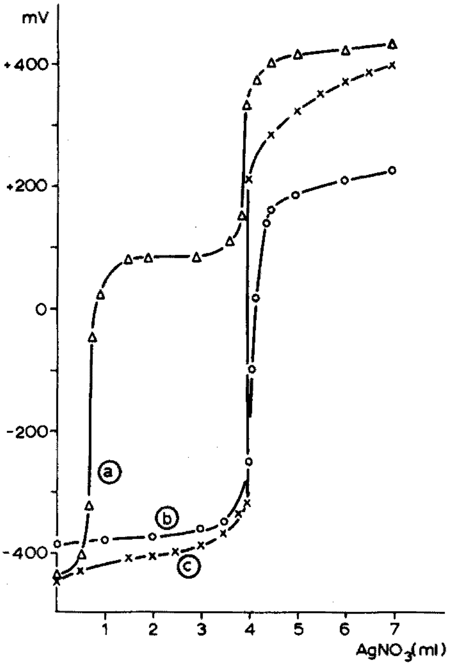
DISCUSSION

As may be seen in Figs. 1–4, thioacetamide can be titrated in the concentration range 10^{-1}–10^{-3} M in distilled water, or in the presence of 0.1 or 1 M sodium hydroxide or in 0.01 M ammonia solution with standard silver nitrate solution. The changes which occur during titration are sensitively followed by the sulphide ion-selective electrode. However, the titration of 10^{-4} M thioacetamide takes a long time in aqueous medium, as the setting up of the equilibrium potential at the electrode is slow at these low concentrations.

In most cases, one potential jump can be observed on the titration curves at a position corresponding to the stoichiometric reaction of thioacetamide with silver nitrate.

The titration curve obtained with 10^{-1} M thioacetamide at pH 12 is different, exhibiting two potential jumps, the second of which can be used for the determination of thioacetamide (Fig. 3).

In order to establish the reason for the first potential jump on curve "a" in Fig. 3, potential and pH measurements were made at constant thioacetamide and varying alkali concentrations (Figs. 5–8).



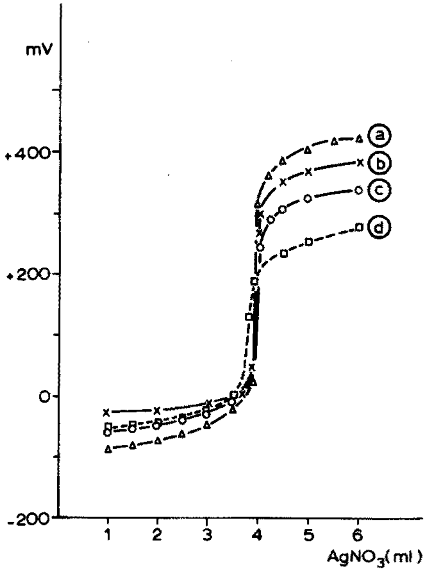


Fig. 3. Potentiometric titration curves of thioacetamide in 10^{-2} *M* ammonia. (a, b, c) As in Fig. 1.

Fig. 4. Potentiometric titration curves of thioacetamide in pure distilled water. (a) 10^{-1} *M* thioacetamide; (b) 10^{-2} *M* Thioacetamide; (c) 10^{-3} *M* thioacetamide; (d) 10^{-4} *M* thioacetamide.

A comparison of the sulphide electrode potential curves with the pH curves shows that the potential of the sulphide electrode changes suddenly at the same volume of standard solution added as a sudden pH change occurs. This is indicative of a remarkable change in sulphide concentration (first potential jumps in Figs. 5 and 7).

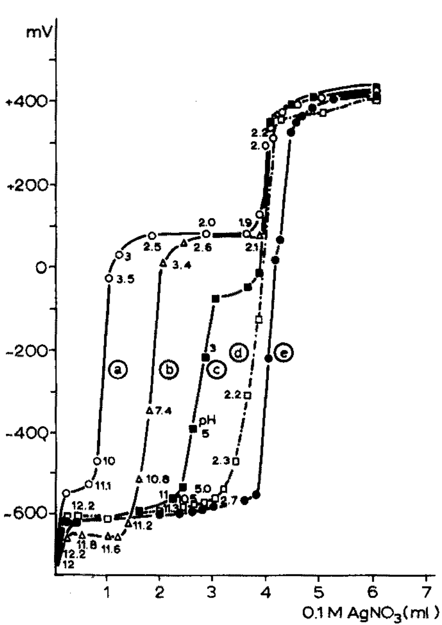
A stoichiometric reaction proceeds also in 0.1 *M* acetic acid. The equivalent weight of thioacetamide is equal to half its molecular weight in these titrations.

In the direct measurement of thioacetamide by means of the sulphide ion-selective electrode, a 30-mV change in electrode potential corresponds to a decade change in thioacetamide concentration in the range 10^{-1} to 10^{-3} *M*, in 0.1 *M* and 1 *M* sodium hydroxide. This also shows that the electrode measures the product of the hydrolysis.

In the presence of 0.1 *M* nitric acid the reaction proceeds in the same way as in alkaline medium or in pure distilled water, *i.e.*, one molecule of thioacetamide reacts with two molecules of silver nitrate. In 0.5 *M* or more concentrated nitric acid solutions, however, a different reaction takes place, and one mole of thioacetamide reacts with only one mole of silver nitrate. In this case the equivalent weight of thioacetamide is equal to its molecular weight.

IDENTIFICATION OF THE PRODUCTS OF TITRATION

In the titration of thioacetamide with silver nitrate in distilled water and in



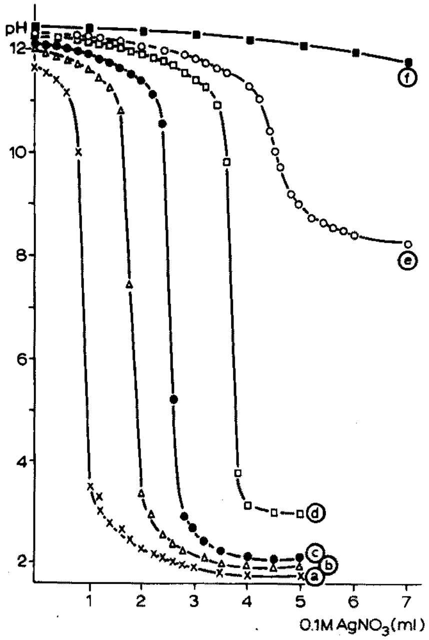
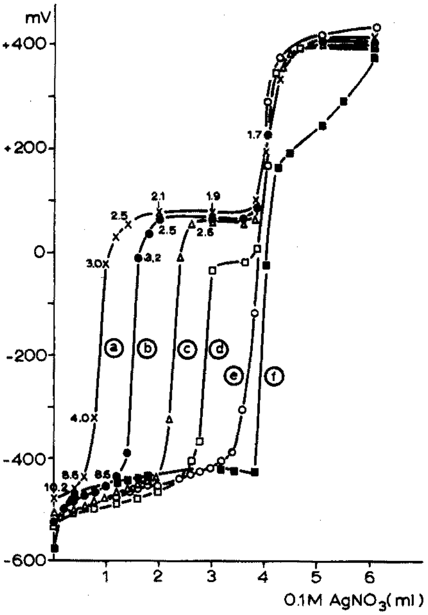


Fig. 5. Potentiometric titration curves of 10^{-1} M thioacetamide in the presence of sodium hydroxide. (a) 0.01 M; (b) 0.02 M; (c) 0.03 M; (d) 0.04 M; (e) 0.05 M; (f) 0.1 M.

Fig. 6. pH titration curves of 10^{-1} M thioacetamide in the presence of sodium hydroxide. (a–f) As in Fig. 5.



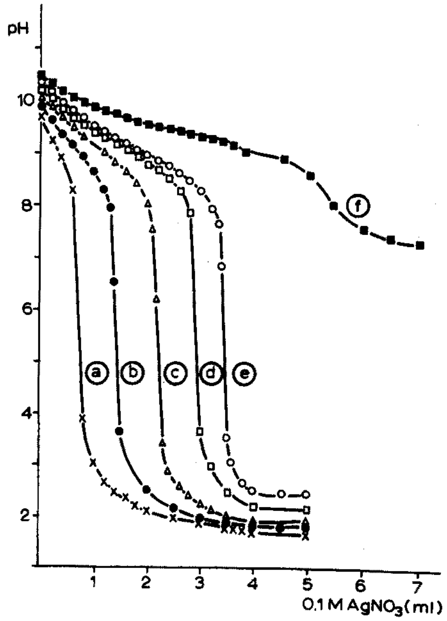
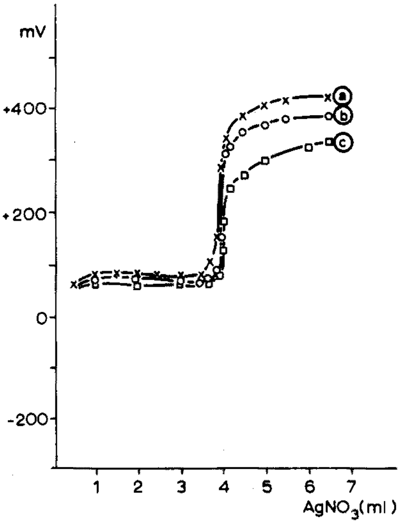


Fig. 7. Potentiometric titration curves of 10^{-1} M thioacetamide in ammonia solution. (a–f) As in Fig. 5.

Fig. 8. pH titration curves of 10^{-1} M thioacetamide in ammonia solution. (a–f) As in Fig. 5.



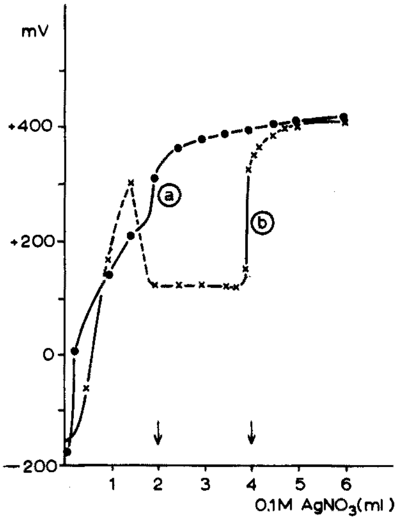
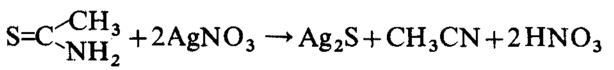


Fig. 9. Potentiometric titration curves of thioacetamide in 10^{-1} *M* acetic acid. (a) 10^{-1} *M* thioacetamide; (b) 10^{-2} *M* thioacetamide; (c) 10^{-3} *M* thioacetamide.

Fig. 10. Potentiometric titration curves of 10^{-1} *M* thioacetamide in 10^{-1} *M* (b) and $5 \cdot 10^{-1}$ *M* (a) nitric acid.

slightly acidic or alkaline solution, a black precipitate was formed. The precipitate was analyzed and found to be silver sulphide.

It is assumed that acetonitrile and nitric acid are formed during the reaction in addition to silver sulphide. Furthermore, the acetonitrile is assumed to hydrolyse giving ammonium acetate, which then in the presence of the nitric acid formed during the reaction transforms to acetic acid and ammonium nitrate according to the following reaction equations:



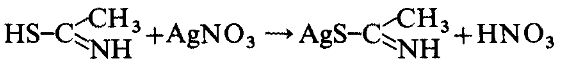
$$\mathrm{S{=}C}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{NH_2}\end{smallmatrix}+2\mathrm{AgNO_3}\rightarrow \mathrm{Ag_2S}+\mathrm{CH_3CN}+2\mathrm{HNO_3}$$

$$\mathrm{CH_3CN}+2\,\mathrm{H_2O}\rightarrow \mathrm{CH_3COONH_4}$$

$$\mathrm{CH_3COONH_4}+2\,\mathrm{HNO_3}\rightarrow \mathrm{CH_3COOH}+\mathrm{NH_4NO_3}+\mathrm{HNO_3}$$

The silver sulphide precipitated in the first step of the reaction was identified by elemental analysis. An ultraviolet spectrum of the filtrate was taken and compared with the spectrum of pure ammonium nitrate, the assumed final product of reaction. The two spectra (Fig. 11) were completely identical.

In 0.5 *M* nitric acid, the reaction of thioacetamide with silver nitrate was entirely different. At a 1:1 molar ratio a light, pearly precipitate was formed. This was identified by elemental analysis and infrared spectroscopy. On this basis the following reaction was assumed to take place in 0.5 *M* nitric acid between the tautomer of thioacetamide and silver nitrate:



$$\mathrm{HS{-}C}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{NH}\end{smallmatrix}+\mathrm{AgNO_3}\rightarrow \mathrm{AgS{-}C}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{NH}\end{smallmatrix}+\mathrm{HNO_3}$$

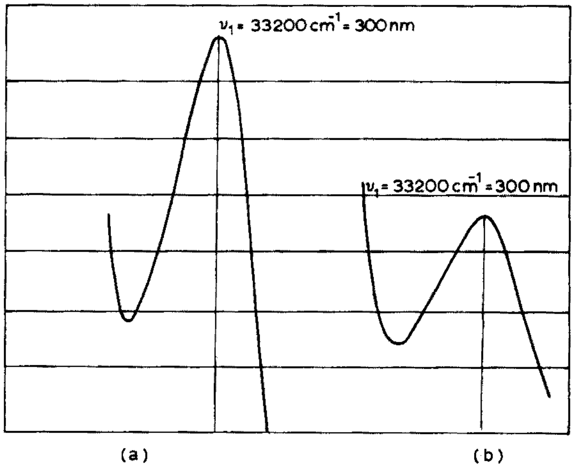


Fig. 11. Ultraviolet spectra of (a) the product of the titration of thioacetamide with silver nitrate formed in addition to silver sulphide; (b) pure ammonium nitrate solution.

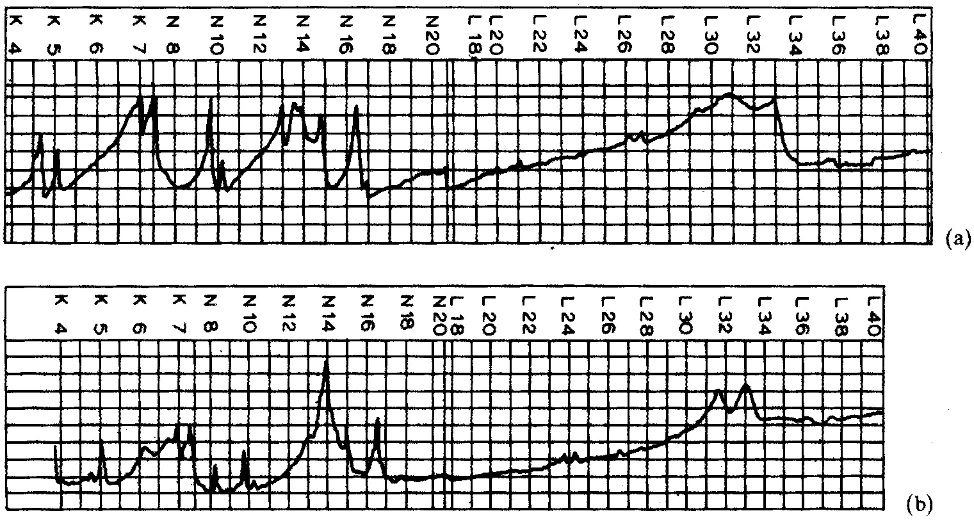


Fig. 12. Infrared spectra of (a) pure thioacetamide; and (b) silver thioacetamide precipitate.

In Fig. 12 are presented the infrared spectra of thioacetamide and of its compound with silver nitrate. The spectra seem to confirm the above reaction, a conclusion also supported by elemental analysis.

SUMMARY

The sulphide ion-selective electrode has been found to be applicable to the determination of thioacetamide in the concentration range of 10^{-1}–10^{-3} M by direct potentiometry and titration with silver nitrate. The effects of the acid and alkali content of the solutions on the titration reaction have been studied. In alkaline and slightly acidic solutions the product of the reaction is silver sulphide; in solutions in which the acid concentration exceeds 0.5 *M*, a precipitate of silver thioacetamide is formed. If the alkali concentration of the solution is lower than that corresponding to the amount of acid formed during the titration, another potential jump occurs before the end-point owing to the decrease of sulphide concentration governed by hydrolysis.

RÉSUMÉ

L'électrode sélective ionique au sulfure peut être utilisée pour le dosage de la thioacétamide en concentrations de l'ordre de 10^{-1} à 10^{-3} *M*, par potentiométrie directe et titrage au moyen de nitrate d'argent. On examine l'influence de l'acidité et de l'alcalinité sur la réaction de titrage.

ZUSAMMENFASSUNG

Die sulfidionen-selektive Elektrode kann für die Bestimmung von Thioacetamid im Konzentrationsbereich 10^{-1}–10^{-3} *M* mittels direktèr Potentiometrie und Titration mit Silbernitrat verwendet werden. Der Einfluss der Säure- und Alkaligehalts der Lösungen auf die Titrationsreaktion wurde untersucht. In alkalischen und schwach sauren Lösungen ist das Reaktionsprodukt Silbersulfid; in Lösungen, in denen die Säurekonzentration 0.5 *M* überschreitet, entsteht ein Niederschlag von Silberthioacetamid. Wenn die Alkalikonzentration geringer ist, als der während der Titration gebildeten Säuremenge entspricht, tritt vor dem Endpunkt ein anderer Potentialsprung auf, der durch die Herabsetzung der durch Hydrolyse bedingten Sulfidkonzentration hervorgerufen wird.

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Analytica Chimica Acta, 64 (1973) 417–421

RECENT RESULTS ON THE DYNAMIC RESPONSE OF PRECIPITATE-BASED ION-SELECTIVE ELECTRODES

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A new method[1] has been elaborated for studying the dynamic response of silver halide-based ion-selective electrodes. The study also involved the examination of silver iodide-based electrodes to cyanide ions. The response curve, *i.e.* the e.m.f. *vs.* time curve, was approximated by an exponential equation.

With regard to electrode kinetics, however, it is important to clarify the chemical and/or physical processes determining the transient signal. The former simulation[1] of the experimental data by an exponential equation led to the conclusion that only one process determines the response time curves as the concentration of the potential-determining ion is instantaneously increased round the electrode. The understanding of the electrode response, however, is more complicated if the concentration change of the appropriate ion is decreasing rather than increasing.

For the theoretical interpretation of the response time curves, some further measurements were carried out with a copper(II)-selective electrode[2]. This electrode is an electronic conductor and its behaviour is quite different from the silver halide-based electrodes studied earlier.

In this paper, the dynamic response of the copper(II)-selective electrode is described, and the theoretical interpretation of the response time curves is discussed generally.

EXPERIMENTAL

Apparatus

A block diagram of the measuring unit is shown in Fig. 1. The measuring cell contained the appropriate heterogeneous silicone rubber ion-selective electrode and a Radiometer saturated calomel electrode Model K 401.

The time constant of the d.c. amplifier was 2 ms; this was measured by means of a square-wave signal.

Procedure

The solution of the potential-determining ion was passed over the ion-selective electrode at such a rate that a continuous thin film on its surface was ensured. The linear flow-rate of the solution was 6 cm s^{-1}. The reference electrode was placed just under the indicator electrode, so that a continuous solution contact was assured during flow. The change in the solution concentration of the potential-

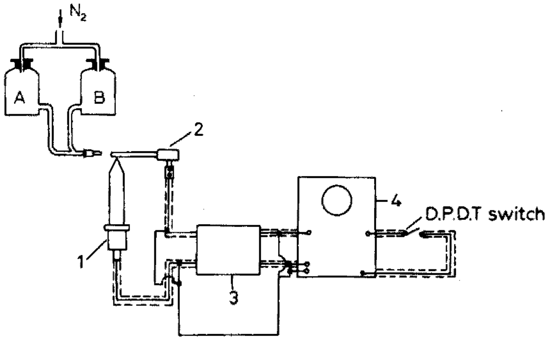

Fig. 1. The block diagram of the measuring device. (A, B) Two different concentrations of the potential-determining ion. (1) Reference electrode; (2) indicator electrode; (3) d.c. amplifier; (4) oscilloscope.

determining ion around the electrode was ensured by interchanging the tubes containing the solutions of the primary ion in front of the electrode with the help of an electro-magnetic unit. The time of the solution change was less than 1 ms, during which the electrode surface was covered continuously with solution.

Variation of the linear flow-rate of the solution within 5–10 cm s^{-1}, was found to have no effect on the transient signal.

Reagents

All reagents used were of *pro analysi* grade.

RESULTS AND DISCUSSION

The effects of the following parameters were studied on the e.m.f. *vs.* time curve of the copper(II)-selective electrode: (1) direction of the concentration jump (Fig. 2); (2) the effect of the concentration level (Fig. 2); (3) the effect of various non-interfering ions (Fig. 3).

In Fig. 2, it can be seen that the direction of the concentration jump has a marked effect on the response time of the ion-selective electrode. This finding is in accordance with the earlier results obtained with halide-based ion-selective electrodes[1]; the response time curve is sharper if the concentration of the appropriate ion is increasing around the electrode, than if the concentration is decreasing. From the curves shown in Fig. 2, it is obvious that the level of the concentration change has no effect on the response time in the concentration range studied.

It is extremely interesting that the effect of the non-interfering electrolyte on the response time curve is negligible or very small in the case of the dehydration, whereas it is marked when hydration takes place at the electrode surface (Fig. 3). The magnitude of the effect of the non-interfering ions, however, depends on the nature of the non-interfering ions. These findings are valid for both halides and copper(II) ions and may be explained by the establishment of a more stable cell potential.

The response time curves which were obtained when the concentration of the potential-determining ion increased round the electrode, can be interpreted as follows.

As a first approximation, an attempt was made to use the desolvation model for the interpretation. It is thus supposed that the ion is built into the crystal skeleton

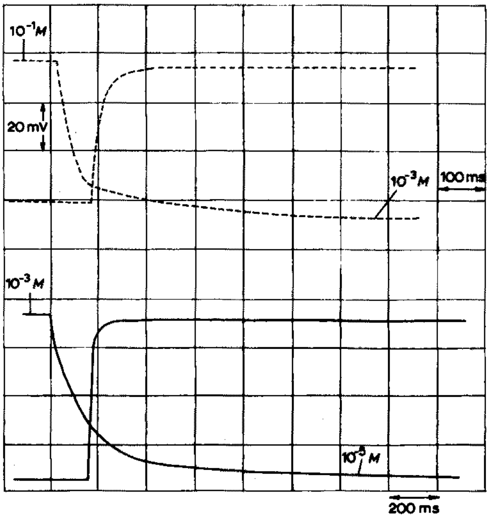

Fig. 2. The effect of the direction of the concentration jump and the concentration level on the e.m.f. *vs.* time curve of the copper(II)-selective electrode (------) $\Delta c_{Cu} = 10^{-1}$–10^{-3} *M*; (——) $\Delta c_{Cu} = 10^{-3}$–10^{-5} *M*.

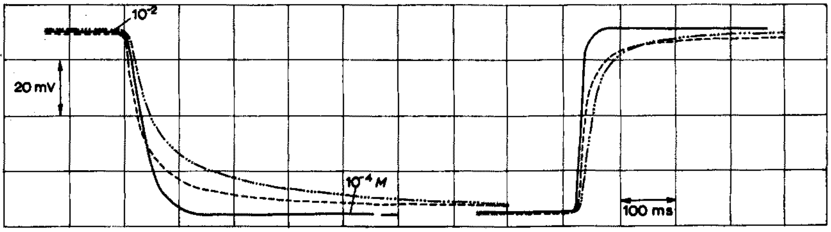

Fig. 3. The effect of non-interfering ions on the e.m.f. *vs.* time curve of the copper(II)-selective electrode. In all cases, $\Delta c_{Cu} = 10^{-2}$–10^{-4} *M*; (——) $+10^{-1}$ *M* KNO_3; (------) $+10^{-2}$ *M* KNO_3; (–·····–····–) no KNO_3.

of the electrode without any solvent shell. If it is assumed that the rate-determining step is the desolvation of ions in the boundary phase of the electrode, an equation can be derived for describing the transient signal.

The desolvation reaction may be written as follows:

$$IS_x \overset{k_1}{\rightleftharpoons} I + xS \qquad (1)$$

where I is the appropriate potential-determining ion, the charge of which is omitted for simplicity; S is the solvent; and x is the mean value of the solvation number.

On the basis of this reaction,

$$d[I]/dt = k_1 [IS_x]_t \qquad (2)$$

where [I] is the concentration of I at the electrode surface produced by the desolvation of the electrolyte introduced; k_1 is the rate constant of the desolvation reaction; and t is time.

$$[IS_x]_t = [IS_x]_0 - [I] \tag{3}$$

Integration of eqn. (2) yields the following equation if it is considered that $[I] = 0$ when $t = 0$:

$$[I] = [IS_x]_0 \cdot (1 - e^{-k_1 t}) \tag{4}$$

The concentration of ion bound on the surface of the electrode is in correlation with the electrode potential, so that eqn. (4) can be rewritten:

$$n \cdot \frac{E_t - E_f}{0.059\,\Delta p(IS_x)} = \log(1 - e^{-k_1 t}) \tag{5}$$

where n is the charge of the primary ion; $\Delta p(IS_x)$ is the difference of the p-values calculated from the activities of the primary ion applied to cause the transient signal; E_t is the potential established at time t; and E_f is the final value of the potential at $t = \infty$.

Hence, one may derive the rate constant of the desolvation reaction:

$$k_1 = -\frac{2.303 \cdot \log\left(1 - 10\,\frac{-\Delta E \cdot n}{0.059 \cdot \Delta p(IS_x)}\right)}{t} \tag{6}$$

The desolvation constants of the iodide and copper(II) ions in distilled water were calculated with the help of eqn. (6). The constants were found to be 4.85 ± 0.2 s^{-1} for iodide, and 20 s^{-1} for copper(II) ion. In the latter case the uncertainty of the determination was higher because of a faster desolvation rate.

The dynamic response time is an important parameter for ion-selective electrodes, especially if they are used for following fast reactions. Accordingly, it is necessary to find a suitable method for the evaluation of the e.m.f. *vs.* time curves. In the literature, among other methods, the time corresponding to 66.6% or 90% of the total potential change has been used as the response time. However, the theoretical considerations discussed earlier give a more exact means of characterizing the dynamic response time of the electrodes by the half-life time of the first-order reactions. This is

$$t_{\frac{1}{2}} = \ln 2/k_1 \tag{7}$$

if the desolvation reaction is considered.

Accordingly, the $t_{\frac{1}{2}}$ value for the iodide electrode is 130 ms, while it is 35 ms for the copper(II)-selective electrode.

A computer program is in preparation, by which the effect of various parameters on the desolvation rate constant will be discussed.

The reaction going in the opposite direction which involves dissolution of the ion from the electrode surface and its solvation, needs further theoretical considerations.

SUMMARY

The e.m.f. *vs.* time curves of the precipitate-based ion-selective electrodes have been interpreted mathematically on the basis of the desolvation of ions at the electrode surface. A new method has been suggested for the characterization of ion-selective electrodes by the half-life time of the first-order desolvation reaction.

RÉSUMÉ

Une étude mathématique est effectuée avec des électrodes sélectives ioniques, basée sur la désolvatation des ions à la surface de l'électrode.

ZUSAMMENFASSUNG

Die EMK–Zeit-Kurven der ionenselektiven Elektroden, bei denen ein schwerlöslicher Niederschlag verwendet wird, wurden auf der Grundlage der Desolvatation der Ionen an der Elektrodenoberfläche mathematisch gedeutet. Eine neue Methode zur Charakterisierung ionenselektiver Elektroden mittels der Halbwertzeit der Desolvatationsreaktion erster Ordnung wurde vorgeschlagen.

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THE CALIBRATION AND RESPONSE OF ION-SELECTIVE ELECTRODES AT LOW CONCENTRATIONS OF PRIMARY IONS

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The rapid growth of the field of ion-selective electrodes in recent years has been remarkable. The range of ions for which there are selective electrodes continues to increase, although now more slowly than before, and the response characteristics of the electrodes are steadily being improved.

As in the early stages of the development of glass electrodes responsive to hydrogen ions, the calibration and use of these electrodes is still very empirical. No conventional standards have yet been established such as are now routinely used in hydrogen ion determination[1]; and there is now a clear need for such conventions, preferably consistent with the conventional pH activity scale. As in the application of the pH scale, it is not necessary, or indeed possible, to be able to deduce accurately from the electrode response the activity of a particular ion in the solution, only to correlate consistently the response of the electrode in solutions of different ionic activity.

From the practical point of view, it is in the lower concentration ranges that the calibration of ion-selective electrodes is most difficult and yet most important, for it is there that the advantages of electrodes over other analytical tools are most striking and their applications most numerous. It has been the practice to calibrate electrodes by repeated dilution of standards; however, although this is satisfactory for high concentrations and down to $10^{-4}-10^{-5}$ M, if sufficient care is taken, below this level the results become increasingly irreproducible. Therefore there has been little reliable information presented on the response of the electrodes below 10^{-5} M in the absence of buffers.

Buffer solutions have been prepared for copper[2,3], silver[4,5], fluoride[6] and the halides[7] based on strong metal complexes or solubility equilibria. The latter are open to the objection that, as they involve heterogeneous equilibria at low concentrations, the rate at which the systems approach equilibrium is necessarily low and they are therefore not useful as buffers. The experiments with electrodes in solutions of metal complexes are interesting insofar as they show the capabilities of the electrodes, but calibration of the electrodes in such solutions containing complexing agents is inappropriate; for, one of the basic principles of electrode calibration, that the calibration standard should be as similar in nature as possible to the sample, is violated. The dissimilarity lies in the buffer capacity of the sample with respect to the ion to be determined; the solutions of these ions are frequently very poorly buffered, unlike the substantial pH buffering usually found. The main use of the electrodes in solutions containing strong complexing agents is as indicator electrodes in potentiometric titrations, in which case electrode calibration is unnecessary.

In the work to be reported here, the responses of silicone-rubber based ion-selective membrane electrodes to low concentrations of primary ion have been studied in various unbuffered media. In particular the failure region of the electrodes was studied. Reproducible and accurately known concentrations of ions were prepared by electrolytic generation. A necessary and integral part of the work was to measure the current efficiency for the generation of the ions in the different media. Results obtained from the calibration of the iodide-ion selective electrode in various media are presented, and results with the silver and copper ion-selective electrodes are briefly discussed.

EXPERIMENTAL

Reagents and instrumentation

All the chemicals used were of analytical-reagent grade ("Reanal", Budapest).

The potentials of the silicone-rubber ion-selective membrane electrodes were measured with respect to a capillary-junction saturated calomel electrode with a Radelkis Model OP-205 pH meter.

A Radelkis Coulometer, Model OH-404, was used for the coulometric determination of the current efficiency of the iodide generation, as described later. The end-point system in the determination was also controlled by the coulometer. The generation of the various ions was done with the coulometer in the constant-current mode.

Methods

Initially and principally, the iodide ion-selective electrode[8] was studied; the standard iodide solutions of low concentration were produced by cathodization of a freshly prepared silver–silver iodide electrode. This latter electrode was prepared with the coulometer as a constant-current source by forming the silver iodide layer on a cleaned silver electrode in a slightly acidic iodide solution[9]. The current efficiency of the generation of iodide into the various media when this electrode was cathodized was measured by coulometric back-titration of the generated iodide ions with silver ions from a silver anode[10]. This method involves the reasonable assumption that the current efficiency for the silver ion generation is 100% in all the media tested. The end-point of the back-titration was determined amperometrically by means of an electrode containing twin silver wires with a potential of 100 mV applied between them. Unfortunately, the rate of equilibration of the end-point system was too slow to permit use of the coulometer in the fully automatic mode, because near the end-point 2–3 min had to be allowed after the passage of each increment of charge before the current became stable. It was thus necessary to find the titration end-point by visually following the ammeter readings: the current reached a minimum at the end-point.

In the later work with the silver-ion selective electrode[10], the silver ions were generated from a silver anode. It was assumed, as in the previous section, that the current efficiency of this generation process was 100%.

In the final and less satisfactory measurements with the generation of copper(II) ions from a copper anode, the final copper(II) ion concentration was higher than the final concentration in the previous work and the generation efficiency could be measured with sufficient accuracy by addition of iodide and titration of the liberated iodide with standard thiosulphate.

The experimental arrangement for the generation and calibration experiments consisted of a generation compartment and an auxiliary compartment. The generation compartment—a 200-ml beaker—contained the ion-selective electrode and the generator electrode immersed in 100 ml of background electrolyte; this solution was stirred magnetically. The auxiliary electrode compartment—a 25-ml beaker—contained the reference electrode and the platinum auxiliary electrode in 0.1 *M* potassium nitrate solution. The two compartments of the cell were joined by an agar–potassium nitrate salt bridge.

At the beginning of each calibration run, the 100-ml background solution was changed and the first two readings of the calibration series were repeated until constant ion-selective electrode potentials were recorded at each point. Usually two such changes were necessary, but more were needed if the electrode had previously been stored in a strong solution of the ion being generated. For each calibration point, an aliquot of charge was passed between the generator electrode and the auxiliary electrode to generate ions into the background electrolyte solution; the charge passed was then read from the digital display on the coulometer and the ion-selective electrode was left to reach equilibrium. At the lowest concentration (10^{-7} *M*), the response was very slow and it was not even certain that equilibrium had been reached after 30 min; however, at higher concentrations the response was much faster. Both the amperometric end-point system of the coulometric titration in the iodide work and the ion-selective electrode responded most slowly in the highest concentration media and most quickly in the 10^{-2} *M* solutions.

RESULTS AND DISCUSSION

Generation of iodide

The current efficiencies measured for the generation of iodide from a silver–silver iodide electrode into the different solutions are presented in Table I. It may be seen that the average current efficiency is always within 0.05% of 100% and is thus sufficiently good for the electrode calibration work. Magno[11] found that the efficiency differed by up to 0.5% from 100% and he ascribed this larger difference to the uncertainty in the definition of the end-point. In the present work the current efficiency in any one determination, when the coulometer's end-point detection system was used at its maximum sensitivity, only very rarely differed by more than 0.1% from 100%. Generation of both the iodide ions and silver ions was carried out at a current density of 0.15 mA cm^{-2} (the current was 1 mA); near the end-point of the titration the current was cut to 0.1 mA.

Both the amperometric end-point system in the efficiency determination and the ion-selective electrode in the calibration were found to respond too slowly in 2 *M* potassium nitrate for useful measurements to be made.

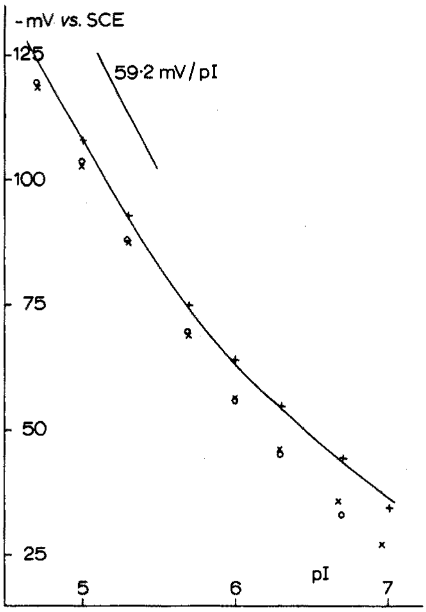
The results of the calibrations in the different solutions are shown in Figs. 1–4, in which are compared the responses of the electrode both in the same electrolyte at different concentrations, and in different electrolytes, including two charge types,

TABLE I

DETERMINATIONS OF THE EFFICIENCY OF THE GENERATION OF IODIDE IONS FROM A SILVER–SILVER IODIDE ELECTRODE

(Iodide concentration generated, $2 \cdot 10^{-5}$ *M*. Solution volume, 100 ml)

Electrolyte	*Concentration (M)*	*No. of determinations*	*Average current efficiency (%)*
$KClO_4$	10^{-1}	2	100.02
	10^{-2}	3	99.96
	10^{-3}	3	99.97
KNO_3	10^{-1}	4	99.97
	10^{-2}	4	100.01
	10^{-3}	4	100.01
$MgSO_4$	1	3	99.97
	10^{-1}	3	100.01
	10^{-2}	4	100.03
	10^{-3}	2	100.04
$ZnSO_4$	10^{-2}	1	99.97
$HClO_4$	10^{-3}	3	99.99



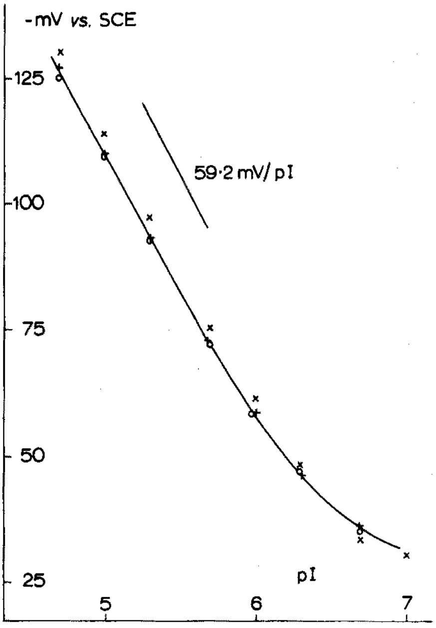
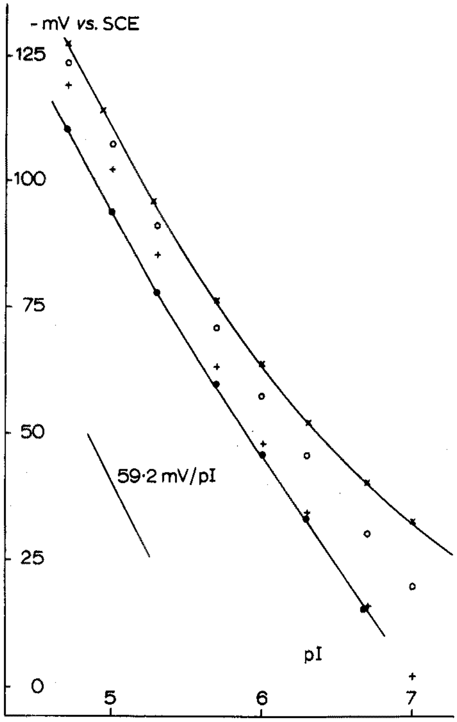


Fig. 1. The calibration of an iodide-selective electrode in different concentrations of potassium perchlorate solution. (+) 10^{-1} *M* $KClO_4$, (×) 10^{-2} *M* $KClO_4$, (○) 10^{-3} *M* $KClO_4$.

Fig. 2. The calibration of an iodide-selective electrode in different concentrations of potassium nitrate solution. (+) 10^{-1} *M* KNO_3; (○) 10^{-2} *M* KNO_3; (×) 10^{3} *M* KNO_3.



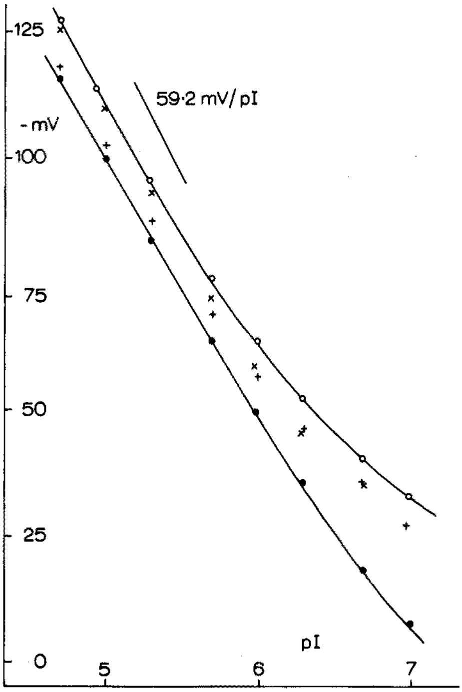


Fig. 3. The calibration of an iodide-selective electrode in different concentrations of magnesium sulphate solution. (●) 1 M $MgSO_4$; (+) 10^{-1} M $MgSO_4$; (×) 10^{-2} M $MgSO_4$; (○) 10^{-3} M $MgSO_4$.

Fig. 4. The calibration of an iodide-selective electrode in different electrolytes at a concentration of 10^{-2} M. The curves have been displaced along the potential axis for easier comparison of the curve shapes. (×) KNO_3; (+) $KClO_4$; (○) $MgSO_4$; (●) $ZnSO_4$.

at the same concentration. There is no significant difference in the shapes of any of these curves. This suggests that adsorption of the electrolyte onto the electrode surface plays little or no part in the electrode response.

The values of pI in the Figures were calulated on the assumption that $pI = -\log c_I$, where c_I is the iodide concentration in the solution deduced by Faraday's law from the quantity of charge passed. The electrode responds not to iodide concentration but to iodide activity; but under the conditions of the experiments, in which the nature and ionic strength of the electrolyte in any given calibration run remain effectively constant, the concentration and activity will be related by a constant factor. Hence a realistic conditional electrode calibration is achieved.

Generation of silver(I)

Silver ions were generated from a silver anode (current density 0.15 mA cm^{-2}) into potassium nitrate solutions of different concentrations, and then monitored with a silver sulphide precipitate-based silicone-rubber membrane electrode. The results are presented in Fig. 5. The results showed excellent reproducibility and the electrode responded linearly with a close to Nernstian slope, down to pAg 6 in all concentrations of the potassium nitrate solution.

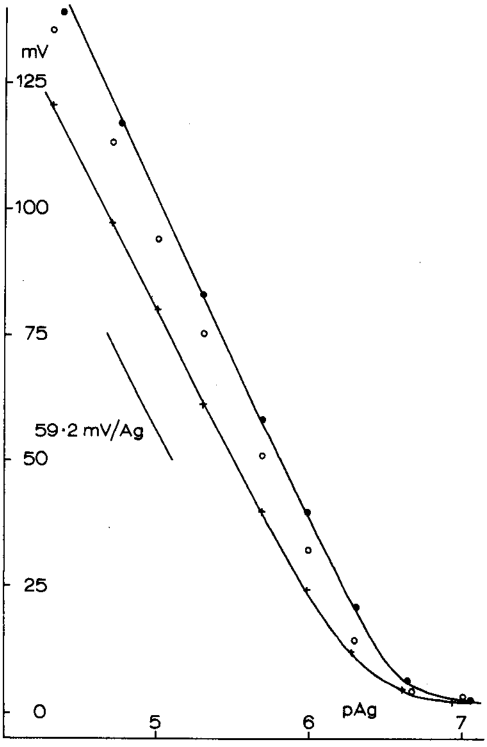


Fig. 5. The calibration of a silver-selective electrode in different concentrations of potassium nitrate solution. The curves have been displaced along the potential axis for easier comparison of the curve shapes. (●) 1 M KNO_3; (+) 10^{-1} M KNO_3; (○) 10^{-2} M KNO_3.

Generation of copper(II)

To examine the response of the copper(II) ion-selective electrode[12], copper-(II) ions were generated from a copper anode. As the efficiency of this process is only *ca.* 90% and is irreproducible, electrode calibration is not possible by this method; however, some information about the response limit of the electrode is obtained. Curves obtained by generation of copper(II) ions into 10^{-2} M potassium perchlorate and 10^{-2} M potassium perchlorate in 10^{-3} M perchloric acid solutions are shown in Fig. 6. It may be seen that the electrode responds well down to a copper concentration of about 10^{-5} M. The pCu values were calculated on the false assumption of 100% generation efficiency.

Conclusions

Many ion-selective electrodes may conveniently be calibrated in the lower concentration ranges, 10^{-4}–10^{-7} M, in standard solutions prepared by electrolytic generation of the appropriate ion. This method has been shown to be applicable to the calibration of iodide and silver ion-selective electrodes; both these ions may be generated into many solutions at a current efficiency of 100%. The response characteristics of the electrodes in the different media may also be studied. Other ions for which there are selective electrodes and which may be electrolytically

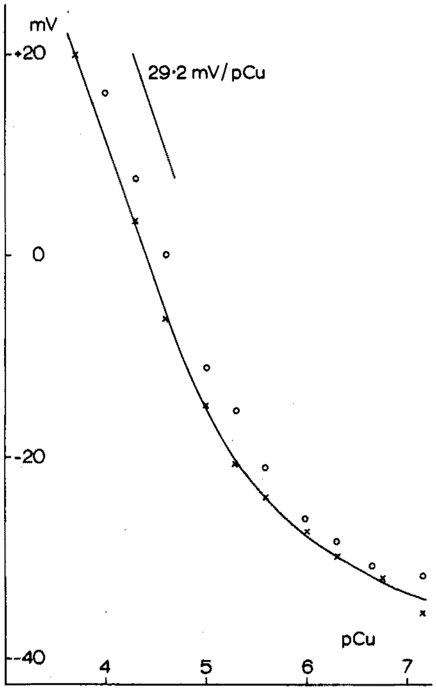


Fig. 6. The response of a copper-selective electrode in different electrolytes. The curve from the calibration in acidic solution has been displaced positively by 20 mV for easier comparison. (×) 10^{-2} *M* $KClO_4$; (○) 10^{-2} *M* $KClO_4$; (——) 10^{-3} *M* $HClO_4$.

generated are sulphide[13], fluoride[14] and thiocyanate[13]: thus it is suggested that this technique is also applicable to them.

The calibration is reliable and easy to do; automation of the whole process would be simple. In a comparison with the dilution technique, it was found that by dilution reproducible results at the lower concentrations were very difficult to obtain, and in no case were the results better than those obtained with the electrolytic generation technique. With this latter technique the careful preparation of a series of solutions and the change of solution and electrode rinsing between each calibration point are unnecessary, and thus much time is saved and many manipulations avoided. Furthermore, the response time of the electrode is effectively shortened as it always remains in the solution and never encounters a sudden concentration jump.

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SUMMARY

Electrolytic generation of ions is proposed for the preparation of standard solutions for the calibration of iodide and silver ion-selective electrodes in the concentration range 10^{-4}–10^{-7} *M*. The responses of these electrodes and also the copper(II) ion-selective electrode were examined in various electrolyte solutions. The current efficiencies of the electrolytic generation of the iodide ions into the various solutions were measured coulometrically. The advantages of this newly proposed calibration technique are discussed.

RÉSUMÉ

La formation électrolytique d'ions est proposée pour la préparation de solutions standards pour le calibrage des électrodes sélectives à ions iodure et argent à des concentrations de l'ordre de 10^{-4} à 10^{-7} *M*. Les réponses de ces électrodes, de même que l'électrode sélective à ion cuivre(II) ont été examinées dans diverses solutions d'électrolytes. Les avantages de cette nouvelle technique de calibrage sont indiqués.

ZUSAMMENFASSUNG

Die elektrolytische Erzeugung von Ionen wird für die Herstellung von Standardlösungen zur Eichung von jodid- und silberionen-selektiven Elektroden im Konzentrationsbereich 10^{-4}–10^{-7} *M* vorgeschlagen. Das Verhalten dieser Elektroden und auch das der kupfer(II)-ionen-selektiven Elektrode in verschiedenen Elektrolytlösungen wurde untersucht. Die Stromausbeuten der elektrolytischen Erzeugung von Jodidionen in den verschiedenen Lösungen wurden coulometrisch gemessen. Die Vorteile dieses neu vorgeschlagenen Eichverfahrens werden diskutiert.

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ION-SELECTIVE CARBON-PASTE ELECTRODES FOR HALIDES AND SILVER(I) IONS

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Electrodes based on solid-state crystals developed by Frant and Ross[1] have received considerable attention[2–5].

The sensing element of most of the ion-selective electrodes in use today is an ion-selective homogeneous membrane (Orion Research-type electrodes) or an ion-selective heterogeneous membrane (Pungor-type electrodes). The heterogeneous membrane contains an electroactive species and inert binder material. As binder, paraffin[6], collodion[7], polyvinyl chloride[8], polyethylene[9] and silicone rubber[10,11] have been used.

Recently, a new type of electrode, the universal ion-selective solid-state electrode has been developed by Ružička and Lamm[12–14]. Whilst the ion-selective electrodes produced previously contained the electroactive species in the bulk of the electrode membrane, the universal ion-selective solid-state electrode has only a superficial layer of the active species rubbed into a compressed paste of graphite and a hydrophobizing material such as teflon. Impregnated graphite rod and carbon pastes have long been used in voltammetry[15–17], as substitutes for noble metal electrodes.

In this paper the behaviour of ion-selective electrodes containing activated carbon paste in a plastic body is described. The electroactive pastes are made from spectral-grade graphite powder, nujol or paraffin wax and metal salts of low solubility. Electrodes consisting of silver chloride, silver chloride–silver sulphide, silver bromide–silver sulphide or silver iodide–silver sulphide with carbon–nujol or carbon–paraffin wax have been investigated. The ion-selective carbon-paste electrodes are suitable for determination of halide ions as well as silver ion in aqueous solutions by direct potentiometric measurement and potentiometric titration.

EXPERIMENTAL

Reagents

Analytical reagent-grade chemicals and twice-distilled water were used in all experiments.

Silver nitrate (0.1 *M*; Titrasol, E. Merck AG) and sodium chloride (0.2 *M*; Titrasol, E. Merck AG) were used. Standard solutions (0.1 *M*) of sodium bromide and potassium iodide were prepared by dissolving the appropriate amounts of the salts

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in water, and standardizing by titration with 0.1 *M* silver nitrate. A 1 *M* sodium sulphide was (freshly) prepared from sodium sulphide monohydrate.

Spectral-grade graphite powder (Le Carbone Lorraine, 45 rue des Acacias, Paris), nujol (paraffin liquid for spectroscopy, E. Merck AG) and paraffin wax (congealing point about 55°, BDH) were also used.

Preparation of the electroactive precipitates

Silver chloride and silver halide–silver sulphide (1:1) were precipitated from 0.1 *M* silver nitrate solution with 0.1 *M* sodium chloride or 0.05 *M* sodium halide + 0.05 *M* sodium sulphide solution. The precipitates were washed with water by decantation, filtered off and dried overnight at 105°. Some precipitates were melted and ground.

All silver solutions and precipitates were shielded from direct light.

Preparation of the ion-selective carbon pastes

First, pure carbon pastes were made by hand-mixing measured quantities of graphite powder and nujol or paraffin wax. The best quality pastes were obtained by mixing carbon and nujol in the ratio 5:1 (w/v) or carbon and paraffin wax in the ratio 3:1 (w/w).

The ion-selective pastes were prepared by mixing measured quantities of electroactive precipitate and pure carbon paste. Pastes with 1% to 30% electroactive material were prepared and studied.

Instrumentation

Potentiometric measurements were made with a Labor pH meter Type 23 (Knick, Berlin) and a flatbed recorder BD 8 (Kipp and Zonen, Delft).

Radiometer titration equipment was used for potentiometric titrations (Radiometer pH meter Type PHM28, Titrator Type TTT11, Autoburette Type AUB12, and Recorder Type SBR2). An Ingold double-junction calomel electrode Type 373-90. M5-NS, filled with 1 *M* potassium nitrate was used as reference electrode. All potentials were recalculated to S.C.E.

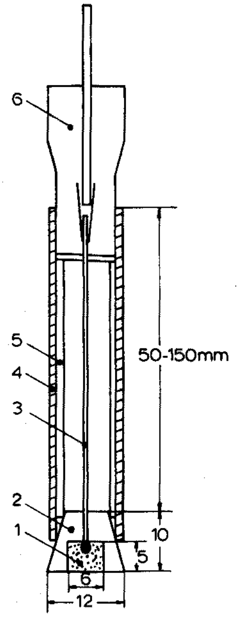
The potentiometric measurements were carried out in the conventional manner and all measurements were performed in a thermostated cell (constant temperature water bath) at 25° ± 0.2°. The solutions were mixed by a magnetic stirrer (Teflon bar).

Construction and preparation of the ion-selective carbon-paste electrodes

Electrode construction—Type 1. A modified Adams pool configuration electrode (as used in anodic stripping voltammetry) proved to be equally useful in potentiometry. The details of the electrode are shown in Fig. 1.

The electrodes were prepared as follows. A well for the paste and a fine borehole for the platinum wire electric connection were drilled in a teflon rod. The teflon plug with platinum wire was connected to a banana plug by means of plastic tubing. A glass tube was inserted to prevent twisting when soft or long plastic tube was used. The active carbon paste was tamped into the well. A smooth paste surface was obtained by smoothing with a plastic spatula or by polishing on a smooth paper, plastic or stainless steel surface.

Electrode construction—Type 2. Figure 2 shows the electrode construction, consisting of plastic material, filled with paste and provided with a screw plunger



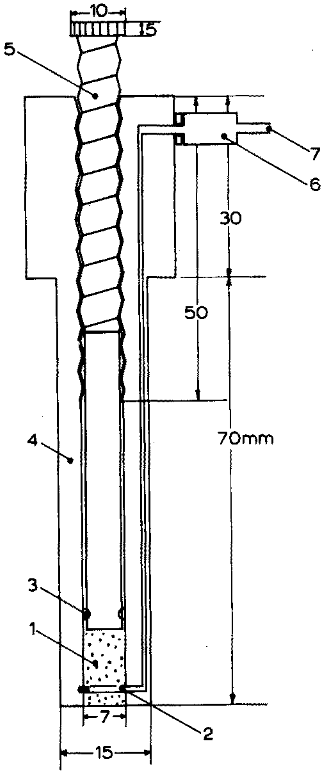


Fig. 1. Electrode construction—Type 1. (1) Paste; (2) teflon plug; (3) platinum wire; (4) plastic tube; (5) glass tube; (6) plug. All dimensions in mm.

Fig. 2. Electrode construction—Type 2. (1) Paste; (2) platinum wire; (3) rubber ring; (4) plexiglass body; (5) screw; (6) banana plug; (7) lead. All dimensions in mm.

by means of which a fresh paste surface could be restored at the lower end of the electrode. The screw could be raised and disconnected by rotating counterclockwise, so that the electrode could be filled with paste (about 0.5–5 g) from the top when the screw was disconnected or from the bottom when the screw was in its higher position. By turning the screw clockwise the paste could be pressed out of the lower end of the electrode. A smooth surface at the lower end was obtained by wiping it with a piece of Kleenex or filter paper and by polishing on a smooth paper, plastic or stainless steel surface.

The paste electrode could be refilled in a few minutes.

RESULTS

Silver chloride and silver chloride–silver sulphide carbon-paste electrodes

Experiments were carried out with 1% and 20% silver chloride, and 1%, 10%, 20% and 30% silver chloride–silver sulphide in carbon–nujol and carbon–paraffin wax pastes.

TABLE I

RESPONSE OF SILVER HALIDE ELECTRODES TO HALIDE IONS

(10% AgX–Ag_2S–carbon–nujol paste electrodes)

C_{X^-}[a]	a_{X^-}[b]	*E (mV) vs. S.C.E.*[c]					
		AgCl		*AgBr*		*AgI*	
		Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
$1\cdot10^{-1}$	$7.7\cdot10^{-2}$	49	47	−102	−101	−325	−315, −318
$1\cdot10^{-2}$	$9.0\cdot10^{-3}$	104	101	−47	−48	−270	−260, −262
$1\cdot10^{-3}$	$9.8\cdot10^{-4}$	161	163	10	11	−213	−201, −197
$1\cdot10^{-4}$	$9.8\cdot10^{-5}$	220	223	69	69	−154	−140, −141
$1\cdot10^{-5}$	$9.8\cdot10^{-6}$	279	263	128	119	−95	−80, −76
$1\cdot10^{-6}$	$9.8\cdot10^{-7}$			187	165	−36	−19, −16
$1\cdot10^{-7}$	$9.8\cdot10^{-8}$					23	69, 42
$1\cdot10^{-7}$	$9.8\cdot10^{-9}$					82	69

[a] C_{X^-} = concentration of Cl^-, Br^- or I^-. [b] a_{X^-} = activity of Cl^-, Br^- or I^-. [c] mV found = average value of three measurements.

TABLE II

RESPONSE OF SILVER HALIDE ELECTRODES TO SILVER IONS

(10% AgX–Ag_2S–carbon–nujol paste electrodes)

C_{Ag^+}	a_{Ag^+}	*E (mV) vs. S.C.E.*			
		Calc.	*AgCl Found*	*AgBr Found*	*AgI Found*
$1\cdot10^{-1}$	$7.4\cdot10^{-2}$	491	472	482	487
$1\cdot10^{-2}$	$9.0\cdot10^{-3}$	437	418	427	432
$1\cdot10^{-3}$	$9.8\cdot10^{-4}$	379	360	374	379
$1\cdot10^{-4}$	$9.8\cdot10^{-5}$	320	299	309	314
$1\cdot10^{-5}$	$9.8\cdot10^{-6}$	261	255	254	254
$1\cdot10^{-6}$	$9.8\cdot10^{-7}$	202		193	195
$1\cdot10^{-7}$	$9.8\cdot10^{-8}$	143		169	139
$1\cdot10^{-8}$	$9.8\cdot10^{-9}$	84			120

The potentials measured and the theoretical potentials for halides and silver(I) with electrodes containing 10% silver chloride–silver sulphide are presented in Tables I and II. A typical electrode response to change in chloride ion concentration (broken line) and activity (solid line) is shown in Fig. 3.

The reproducibility of the potentials for different solutions of the same chloride or silver ion concentration was within ±1 mV. The numerical values for the same solution, obtained with pastes containing different percentages of active material, did not deviate by more than 10 mV from each other. Electrodes with such low concentrations as 1% silver halide were satistactory when freshly prepared, though slower in response than electrodes containing more active material; but such electrodes are more liable in the long run to interference from formation of precipitates on the surface.

The silver chloride as well as the silver chloride–silver sulphide carbon-paste electrodes showed Nernstian response to chloride and silver ion activity as low as $5 \cdot 10^{-5}$ *M*. However, the potential values at chloride or silver ion concentrations below $5 \cdot 10^{-5}$ *M* varied from electrode to electrode, as well as from measurement to measurement.

Electrode potentials were attained rapidly. In general, in solutions above $1 \cdot 10^{-3}$ *M* the potential became stable (to ±1 mV) after 0.2–1 min and below this concentration after 5–10 min.

The influnce of pH on the potential of the electrode in $1 \cdot 10^{-3}$ *M* sodium chloride was studied. It was shown that nitric acid up to 1.5 *M* and sodium hydroxide up to 0.1 *M* do not interfere.

Silver bromide–silver sulphide and silver iodide–silver sulphide ion-selective carbon-paste electrodes

The behaviour of 1%, 10% and 20% silver bromide–silver sulphide and 1%, 10% and 20% silver iodide–silver sulphide carbon–nujol pastes was investigated. It was found useful to melt the active precipitates in order to obtain stable potentials.

The electrode responses to change in bromide, iodide and silver ion activity are presented in Tables I and II. The silver bromide–silver sulphide electrodes showed Nernstian response to bromide and silver ion concentration down to about $1 \cdot 10^{-5}$ *M*. The silver iodide–silver sulphide electrodes showed Nernstian response to iodide and silver ion concentrations down to as low as $5 \cdot 10^{-7}$ *M*. The potentials below these values varied and will be discussed below. Generally, the behaviour of the bromide or iodide electrodes was similar to the carbon-paste electrodes activated with silver chloride.

These ion-selective carbon-paste electrodes can, like other silver halide-based electrodes, serve as sensitive end-point detectors in potentiometric precipitation titration of silver or halides. The equivalence-point potentials are presented in Table III. Excellent results were obtained in potentiometric titrations of mixtures of iodide, bromide and chloride. The titration curve of a mixture of $5 \cdot 10^{-4}$ *M* sodium chloride, sodium bromide and potassium iodide is shown in Fig. 4.

TABLE III

SOLUBILITY PRODUCTS AND EQUIVALENCE-POINT POTENTIALS OF SILVER HALIDES

	AgCl	*AgBr*	*AgI*
Solubility product[18]			
K	$1.72 \cdot 10^{-10}$	$3.3 \cdot 10^{-13}$	$8.5 \cdot 10^{-17}$
p*K*	9.75	12.31	16.06
Equivalence-point potential			
Calc. mV *vs.* S.C.E.	270	194	83
Found mV *vs.* S.C.E.	273	199	96

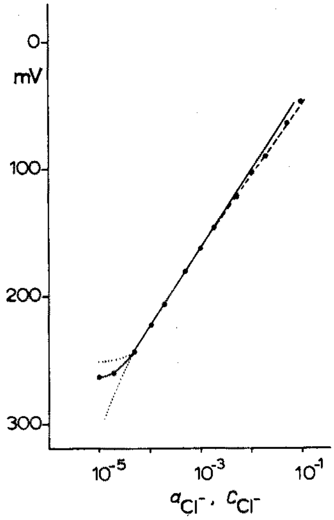


Fig. 3. Calibration curve of chloride electrode. a_{Cl^-} (solid line), C_{Cl^-} (broken line).

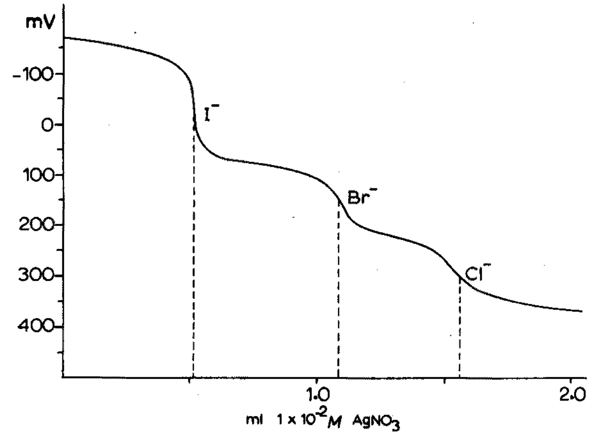


Fig. 4. Titration curve of $5.0 \cdot 10^{-4}$ M NaCl, $5.1 \cdot 10^{-4}$ M NaBr and $5.05 \cdot 10^{-4}$ M KI (10 ml) with $1.0 \cdot 10^{-2}$ M $AgNO_3$. As indicator electrode served the 10% AgI–Ag_2S–carbon–nujol electrode.

DISCUSSION AND CONCLUSION

The potential of the silver halide carbon paste is governed by the silver ion activity, but this in turn depends on the halide ion activity via the solubility product of the silver halide.

The limit of detection of the electrodes is a function of the solubility[4,16] of the immobilized precipitate.

At very low levels of the free halide or silver(I) ions (Fig. 3, dotted lines), the activated carbon-paste electrodes suffered from subsensitivity and supersensitivity (see ref. 12). However, the same data were obtained when the electrode was resurfaced between runs.

In normal usage, numerous determinations of chloride, bromide, iodide as well as silver could be made at the various concentration levels, over a period of several months without the necessity of renewing the electrode surface.

The activated carbon electrodes are suitable for determinations of halide or silver (concentration, or activity) by applying direct potentiometric measurements in any of the usual ways, or by a potentiometric precipitation titration.

Potentiometric titrations offer an increase in accuracy and precision. However, mixtures of halides cannot be titrated as accurately as a single halide[19]. The silver halides have a great tendency to coprecipitate. A positive error in the end-points for iodide and bromide was found with a mixture which was $5 \cdot 10^{-4}$ M in each of chloride, bromide and iodide (Fig. 4).

In the paste surface, a sufficiently small cavity for the test solution was easily formed, so that the potentiometric determinations could be carried out in submillilitre volumes.

The potential-determining mechanism for these electrodes involves an ion-exchange process between the test solution and the surface layer of the active precipitate phase, with carbon acting as an inert electron collector or donor (*cf.* Ružička *et al.*[12,14]). The ion-selective carbon paste electrode dipped into a solution of an oxidizing agent showed a certain potential in the establishment of which the carbon itself has no part. The more strongly oxidizing the solution (Fe^{3+}, $KMnO_4$, Ce^{4+}, etc.), the more positive was the potential. Compounds having a strong oxidizing action interfered and should therefore be reduced or complexed beforehand.

SUMMARY

The behaviour of a simple type of ion-selective electrode for halogens and silver has been studied. The electrode consists of a plastic body filled with carbon paste, the surface of which can be easily renewed. The paste composition is based on carbon–nujol (5:1, w/v) or carbon–paraffin wax (3:1, w/w) containing a prepared mixture of silver halide–silver sulphide (1–30%). The electrodes have low ohmic resistance and show a rapid Nernstian response (within 2–5 mV) for halide and silver ions down to $5\cdot10^{-5}$ *M* chloride, $1\cdot10^{-5}$ *M* bromide and $5\cdot10^{-7}$ *M* iodide with the respective electrodes. Ions forming very stable complexes with halide or silver and those having strong oxidizing or reducing action interfere.

RÉSUMÉ

Une étude est effectuée sur le comportement d'une électrode sélective ionique, de type simple, pour halogènes et argent. L'électrode est constituée d'un corps de plastique rempli d'une pâte de carbone, dont la surface peut être facilement renouvelée. La composition de la pâte est à base de carbone–nujol (5:1 poids/volume) ou de carbone–paraffine (3:1 poids/poids) avec 1 à 30% d'un mélange halogénure d'argent–sulfure d'argent. L'électrode présente une faible résistance ohmique et une réponse nernstienne rapide. Les ions formant des complexes très stables avec halogénure ou argent, et ceux ayant une action fortement oxydante ou réductrice gênent.

ZUSAMMENFASSUNG

Das Verhalten eines einfachen Modells einer ionenselektiven Elektrode für Halogene und Silber wurde untersucht. Die Elektrode besteht aus einer Kunststoffhülle, die mit einer Kohlepaste gefüllt ist, deren Oberfläche leicht erneuert werden kann. Die Paste enthält Kohlenstoff–Nujol (5:1, G/V) oder Kohlenstoff–Paraffinwachs (3:1, G/G), dem 1–30% Silberhalogenid–Silbersulfid beigemischt sind. Die Elektroden haben einen niedrigen Ohmschen Widerstand und zeigen ein schnelles Nernstsches Ansprechverhalten gegenüber Halogenid- und Silberionen. Die unteren Konzentrationsgrenzen für die entsprechenden Elektroden sind $5\cdot10^{-5}$ *M* Chlorid, $1\cdot10^{-5}$ *M* Bromid und $5\cdot10^{-7}$ *M* Jodid. Ionen, die mit Halogenid oder Silber sehr stabile Komplexe bilden oder stark oxidierend oder reduzierend wirken, stören.

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AN ENZYME ELECTRODE FOR THE AMPEROMETRIC DETERMINATION OF GLUCOSE

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The importance of accurate glucose determinations for the diagnosis and treatment of diabetes and other medical problems has been well recognized. Before the twentieth century, over thirty methods for the measurement of glucose in biological fluids had been devised[1]. The desire for simplicity, precision and good selectivity has brought about the development of several hundred methods and modifications within the past several decades. As a result of this wealth of data on methods for determinations of glucose, several reviews have been published[1–6].

A decade ago the most commonly used methods depended on the aldehydic character of glucose to reduce salts of certain heavy metals and nitro-aromatic acids. Spectrophotometric methods were then used to detect the products formed. More recently enzymatic techniques have been developed in order to increase the specificity. Many of these methods involve the coupled glucose oxidase–peroxidase enzyme system shown in reactions (1) and (2):

$$\text{glucose} + O_2 + H_2O \xrightleftharpoons{\text{glucose oxidase}} \text{gluconic acid} + H_2O_2 \tag{1}$$

$$\text{chromogenic oxygen acceptor} + H_2O_2 \xrightarrow{\text{peroxidase}} \text{chromogen} + H_2O \tag{2}$$

where peroxidase catalyzes the transfer of oxygen from hydrogen peroxide to a chromogenic oxygen acceptor. A few of the chromophores that have been used are: *o*-tolidine[7], *o*-dianisidine[8], homovanillic acid[9], 2,6-dichlorobenzenone-indophenol[10], and guaiacol[11].

The trend toward automation and simplification of the analysis of blood components has led to the development of several electrochemical methods; most involve an enzyme-catalyzed system and the rate of the reaction is measured. Potentiometric methods include a null-point method based on the reaction of iodide with the hydrogen peroxide to form iodine[12] and a pH-stat method[13]. Other electrochemical methods include the constant-current monitoring of hydrogen peroxide, with diphenylaminesulfonic acid as an initial potential poiser[14], the monitoring of oxygen used up in the reaction with an oxygen sensor[15,16], the differential amperometric measurement of hexacyanoferrate(III) produced by peroxide oxidation[17,18], and the monitoring of the electro-oxidation of hydroquinone formed as a product of the reaction when the oxygen is replaced with benzoquinone[19].

Several patents have been filed that utilize electrodes of a biochemical type. One uses an amperometric oxygen electrode over which a gelatinous membrane of an enzyme is placed[20]. Another uses an amperometric device whereby an inactive material is converted to an active one by one or more enzymes and determined amperometrically[21]. A third measures elements of an enzyme-substrate system wherein the reaction product has a conductivity different from that of the substrate[22]; the variation in current flow between two electrodes in a predetermined period of time is measured.

This paper describes an enzyme electrode method for the determination of glucose by direct amperometric measurement of the hydrogen peroxide produced. The enzyme electrode is constructed by placing a thin immobilized layer of glucose oxidase (EC 1.1.3.4 from *Aspergillus niger*) around a platinum or special thin film electrode. When this electrode is placed in a glucose solution, glucose diffuses into the gel layer where it undergoes reaction (1). The hydrogen peroxide produced then diffuses towards both the sensing surface and the solution, the rate of production being followed amperometrically by the electrode.

The main purpose of constructing such a glucose electrode was to develop a method for the determination of glucose in biological fluids, especially blood, that would be rapid, reliable, simple and economical enough to be applied on the spot in the physician's office or small clinical laboratory. The glucose electrode method was compared directly to the widely used Dubowski (*o*-toluidine) method.

EXPERIMENTAL

Apparatus

A Heath Polarograph System (Model EUA-19-2) was used. For the hydrogen peroxide study the system was used as a three-electrode polarograph with platinum electrodes (Beckman Model 39273 and 39271) and a commercial saturated calomel electrode. For the glucose electrode study it was used as a two-electrode polarograph with constant potential.

Reagents

All buffers were made at an ionic strength of 0.1, unless specified otherwise, with reagent-grade chemicals. Stock solutions of hydrogen peroxide were prepared from a 30% solution (Mallinckrodt). Stock solutions of glucose were prepared with β-D(+)glucose (Sigma Chemical Co.) and allowed to equilibrate overnight. Reagents used for the application to blood samples include an AQC Set (Dade) and Moni-Trol II (Dade) for blood glucose controls, and an *o*-toluidine reagent (Sigma Chemical Co.). Glucose oxidase was purified from *Aspergillus niger* (Sigma Chemical Co., Type II, 18,000 EU/g). The cellophane was 25-μm thick dialysis tubing (Will Scientific, Inc.). The sensors used in the glucose electrode were either commercial platinum electrodes or a specially constructed electrode consisting of a thin catalytic glassy platinum film painted on glass (Owens-Illinois, Toledo, Ohio). All water was doubly distilled in glass.

Pretreatment of electrodes

Platinum electrodes for the hydrogen peroxide study were pretreated before each run by applying a negative potential (−0.2 V *vs.* S.C.E.) until the cathodic current decayed to a low value, then a slightly anodic potential (0.05 V *vs.* S.C.E.) until the current decayed close to zero. The glucose electrodes were pretreated before use by applying a potential of 0.6 V *vs.* S.C.E. until the anodic current decayed to a low value. After each run the glucose electrodes were washed in a stirring buffer solution until the current decayed to a low value (0.5–1 min) indicating the removal of unreacted glucose and the reaction products.

Application to blood analysis

The glucose electrode method was compared directly to the widely used Dubowski (*o*-toluidine) method and indirectly to the Folin–Wu and Nelson–Somogyi methods. The samples used were from an Accuracy in Quality Control (AQC) Set (Dade) which consists of two controls, one (Lab-Trol) containing known values of serum protein, organic and inorganic substances in the normal range, and the other (Patho-Trol) containing known values in the abnormal range. By using various ratios of these, eleven samples with various glucose levels were made. Assay values were given for glucose by the Folin–Wu and Nelson–Somogyi methods.

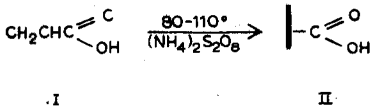
Preparation of physically bound glucose oxidase electrodes

Type 3 electrodes were prepared by placing powdered glucose oxidase between the electrode and a cellophane layer, holding the cellophane in place with a rubber "O" ring. This electrode was then placed in a buffer solution for a few days to allow penetration of buffer into the enzyme layer and loss of trapped air. Type 2 electrodes were prepared by physically entrapping glucose oxidase in a polyacrylamide gel matrix over the electrode. The electrode was first covered with a thin nylon net (about 89 μm thick) which was secured with a rubber "O" ring. This served as a support for the enzyme gel solution. The enzyme gel solution was prepared by mixing 0.1 g of glucose oxidase with 1.0 ml of gel solution. The gel solution was prepared by dissolving 1.15 g of N,N'-methylenebisacrylamide (Eastman), 6.06 g of acrylamide monomer (Eastman), and 5.5 mg of riboflavin in 50 ml of water. The electrode and net were covered with a thin film of the enzyme gel solution. The electrode was then placed in a water-jacketed cell at 0–5°. Oxygen inhibited the polymerization and was removed by purging with nitrogen before and during polymerization. Polymerization was then completed by irradiating with a 150-W Westinghouse projector spot light for 1 h. After polymerization the electrode was soaked in buffer solution for several days.

Preparation of chemically bound glucose oxidase electrodes

Type 1 electrodes were prepared by trapping a thin layer of chemically bonded glucose oxidase between the electrode and a layer of cellophane secured with a rubber "O" ring. Two types of chemical binding were used. One involved the formation of a hydrazide derivative of polyacrylamide which was converted to an acyl azide intermediate that couples to amine groups on the enzyme as described by Inman and Dintzis[23]. The second method involved the coupling of a diazo derivative of polyacrylic acid to the enzyme as shown in reactions (3)–(7).

Acrylic acid (Aldrich) was polymerized by heating with a few milligrams of ammonium persulfate at 80–110° for several hours. The viscous polyacrylic acid formed (II) was then saturated with an excess *p*-nitroaniline by stirring overnight. A portion of this was then diluted with an equal part of water. The nitro group on (III) was then reduced by adding titanium trichloride (26%) dropwise with



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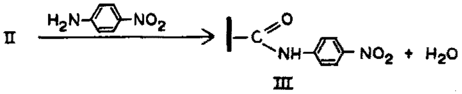

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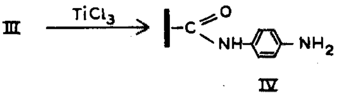

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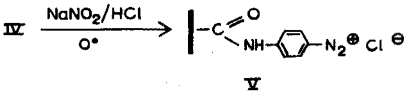

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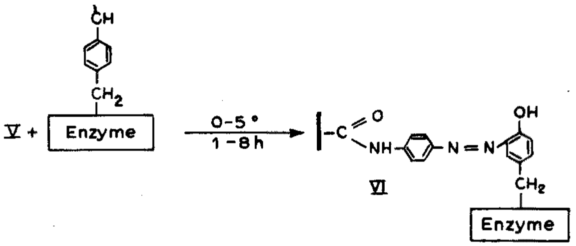

(7)

vigorous stirring. When reduction was complete, the yellow-orange color of (III), which was soluble, was completely changed to a blue-black precipitate (IV). The precipitate was then washed several times with water and then cold (0°) 2 *M* nitrous acid was added slowly with vigorous stirring until the blue-black polymer (IV) completely turned white. The diazonium derivative formed (V) was quickly washed several times with cold 0.1 *M* phosphate or acetate buffer pH 6.0. A cold glucose oxidase solution was then added and the mixture was stirred for 1–8 h in an ice-bath, after which the precipitate was washed several times with cold buffer solution.

Procedures

Colorimetric assay of glucose. The *o*-toluidine procedure used was that described by Sigma Chemical Co.[24]. Tubes containing a mixture of 5.0 ml of *o*-toluidine reagent and 0.1 ml of sample were placed in a vigorously boiling water-bath for exactly 10 min after which all tubes were quickly removed and cooled to room temperature by placing in tap water for 3 min. The absorbance of each sample was then read within 20 min at 635 nm using a blank as reference.

Glucose electrode assay. The glucose electrode procedure consisted of placing the electrode which was poised at a potential of +0.6 V *vs.* S.C.E. into a quiescent solution containing a mixture of 0.1 ml of sample and 1.0 ml of phosphate buffer, pH 6.6. The initial rate of change in current, or the steady-state current at 1 min, was then measured.

RESULTS AND DISCUSSION

Hydrogen peroxide response

The anodic and cathodic decomposition of hydrogen peroxide has been the subject of much investigation for over a century. Hickling and Wilson[25] studied the anodic decomposition of hydrogen peroxide at platinum, gold, nickel, and graphite electrodes and indicated that the oxidation of hydrogen peroxide at a platinum electrode could form the basis of a direct coulometric determination of hydrogen peroxide. This was accomplished when Harrar[26] developed a controlled-potential coulometric method involving the oxidation of hydrogen peroxide at 0.93 V (*vs.* S.C.E.). Raspi and Nucci[27] demonstrated the feasibility of the determination of hydrogen peroxide by means of its reduction at a platinum electrode. Current intensities of the cathodic waves were proportional to the hydrogen peroxide concentration and quantitative determinations down to $1 \cdot 10^{-5}$ *M* were possible. Pellequer[28] demonstrated that the polarographic method is capable of detecting as little as 1 μg of hydrogen peroxide in 2 ml of sample.

The effect of pH on the anodic current–voltage curve of hydrogen peroxide is shown in Fig. 1. As the pH of the solution is decreased, the oxidation wave becomes more anodic. This behavior is expected from the oxidation scheme of hydrogen peroxide at pH 0–11.6 given by the equation:

$$H_2O_2 \rightarrow O_2 + 2\,H^+ + 2e^- \tag{8}$$

Similar correlation was obtained for cathodic waves[27]. In the pH range 0–11.6 the shift is *ca.* 60 mV per pH unit change. When applied to enzyme systems, the realization of this pH dependence is important. Since the pH at which various enzymes are active varies over a wide range, the coupling of hydrogen peroxide detection to the system requires a knowledge of the position of the diffusion current plateau for a particular pH and buffer.

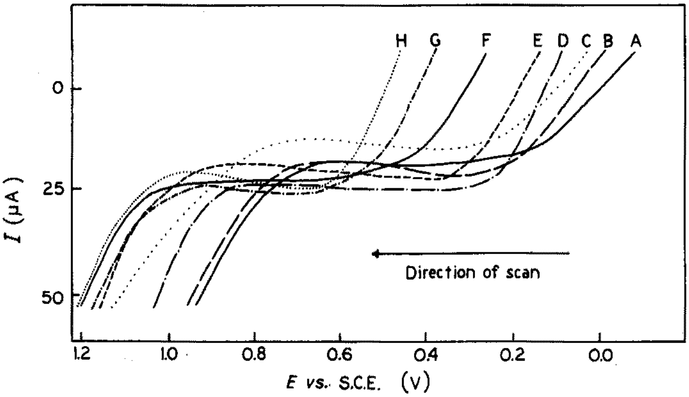

Fig. 1. Family of current–potential curves for the pH dependence of hydrogen peroxide at a platinum electrode. $C_{H_2O_2} = 4.84 \cdot 10^{-3}$ *M*; scan rate = 200 mV min^{-1}; quiescent buffer solutions (ionic strength = 0.1). A = glycine, pH 11; B = glycine, pH 10; C = glycine, pH 9; D = phosphate, pH 8; E = phosphate, pH 7; F = phosphate, pH 6; G = acetate, pH 5; H = acetate, pH 4.

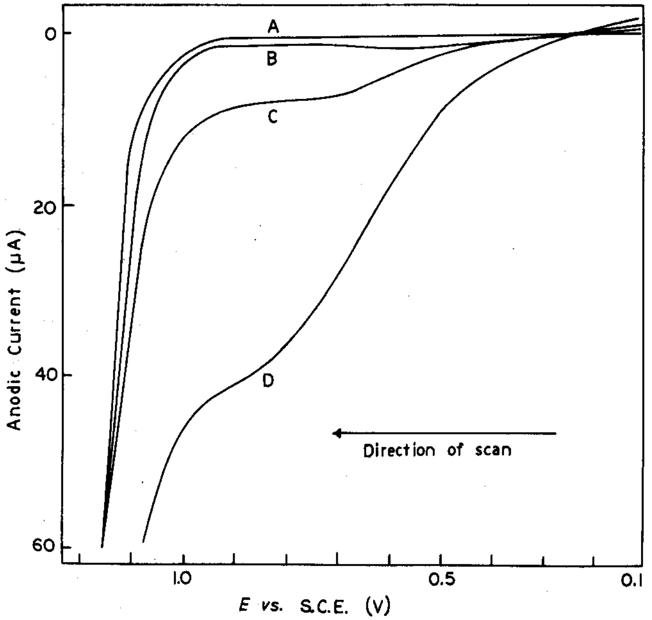

Fig. 2. Family of current–potential curves for the concentration dependence of hydrogen peroxide at a platinum electrode. 1.0 *M* KCl; scan rate = 200 mV min^{-1}; quiescent solutions of H_2O_2. A = Residual current; B = $9.68 \cdot 10^{-6}$ *M*; C = $9.68 \cdot 10^{-5}$ *M*; D = $4.84 \cdot 10^{-4}$ *M*.

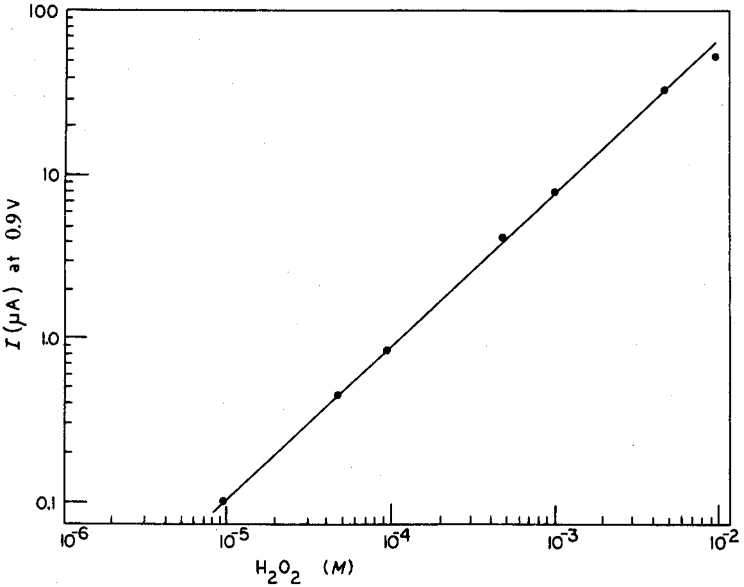

Fig. 3. Calibration curve for hydrogen peroxide.

Typical current–voltage curves of various concentrations of hydrogen peroxide in 1.0 *M* KCl are shown in Fig. 2. Although the hydrogen peroxide waves are quite irreversible, the diffusion current is well defined and was used for its deter-

TABLE I

RESULTS OF THE DETERMINATION OF HYDROGEN PEROXIDE[a]

H_2O_2 molarity		*Current (μA)*	*Relative error (%)*
Added	*Found*		
$9.68 \cdot 10^{-6}$	$9.56 \cdot 10^{-6}$	1.0	1.2
$4.84 \cdot 10^{-5}$	$4.78 \cdot 10^{-5}$	4.5	1.3
$9.68 \cdot 10^{-5}$	$9.54 \cdot 10^{-5}$	8.6	1.4
$4.84 \cdot 10^{-4}$	$5.07 \cdot 10^{-4}$	41.0	4.7
$9.68 \cdot 10^{-4}$	$1.02 \cdot 10^{-3}$	79.0	5.5
$4.84 \cdot 10^{-3}$	$4.56 \cdot 10^{-3}$	320.1	5.8
	Av. rel. error		3.3%

[a] Values at 30°.

mination. Calibration curves obtained in various electrolytes are similar to the one shown in Fig. 3. The current produced at 0.9 V *vs.* S.C.E. by various concentrations of hydrogen peroxide in 0.1 *M* KCl was measured from the current–voltage curves. The voltage sweep rate was +0.2 V min^{-1} and the solution was stirred. A wide range of concentrations can be detected without dilution because it is possible to record a wide range of currents by changing a dial setting. In Table I the concentrations found and the relative errors are given for the linear portion of the curve in Fig. 3. The average relative error was 3.3% in the 10^{-5}–$5 \cdot 10^{-3}$ *M* range.

Glucose electrode response

Typical response curves of the glucose electrode are shown in Fig. 4. When

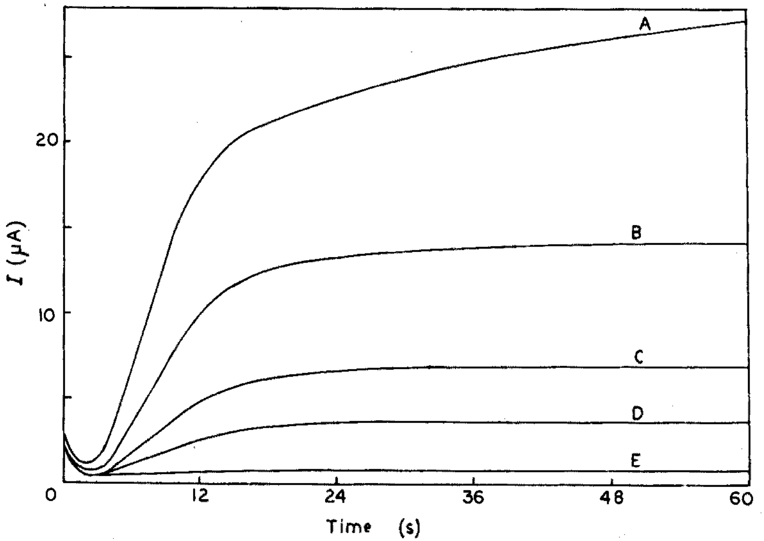

Fig. 4. Family of current–time curves for the glucose electrode poised at 0.6 V. Glucose solutions are in phosphate buffer, pH 6.0; ionic strength 0.1. A=$2.0 \cdot 10^{-2}$ *M*; B=$1.0 \cdot 10^{-2}$ *M*; C=$5.0 \cdot 10^{-3}$ *M*; D=$2.5 \cdot 10^{-3}$ *M*; E=$5.0 \cdot 10^{-4}$ *M*.

an electrode is placed in a glucose solution the current initially decreases for about 2 s, because of the diffusion of the glucose through the cellophane and/or enzyme gel layers. The lower concentrations would seem to give very low values and thus low precision, but these curves were put on the same scale only for the purpose of comparison. It should be remembered that one only needs to increase the sensitivity by turning the dial on the ammeter. If this is done, the curves for lower concentrations will have the same shape and height as those of higher concentrations. When used for the determination of blood glucose, the situation is different. The concentrations do not vary over several decades and thus a single scale can be accurately used with the highest expected concentration giving a steady-state value near the top of the recorder or meter scale.

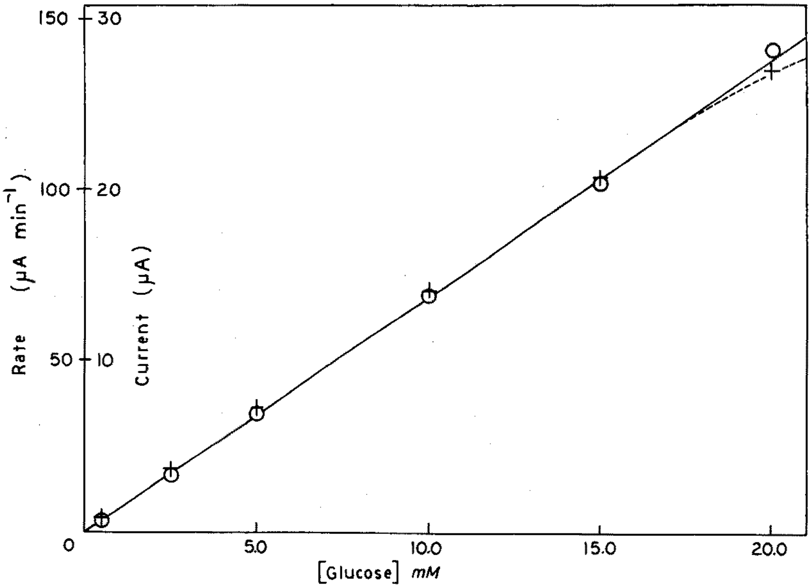

Fig. 5. Calibration curve for glucose. + = Steady-state current method (current axis, μA); ○ = reaction rate method (rate axis, μA min^{-1}).

Two different methods of analysis have been used successfully, initial rate and steady state. Both the initial rate of reaction (within 4–12 s) and the steady-state current (at 1 min) give good calibration curves (Fig. 5). Reproducibility of the measurements was less than 2% for the rate measurements and less than 1% for the steady-state measurements. The error obtained by fitting the points to a linear least-squares analysis was 1.9% for the rate-calibration curve and 2.1% for the steady-state curve. When interferences are present that give a significant background current, the rate method would be the method of choice, because background current has no effect on the measurement of a rate. The steady-state current method can also be used successfully if another electrode similar to the enzyme electrode but without the enzyme is used in parallel with the enzyme electrode and its response subtracted from the glucose electrode response by means of a differential amplifier or some other subtracting technique.

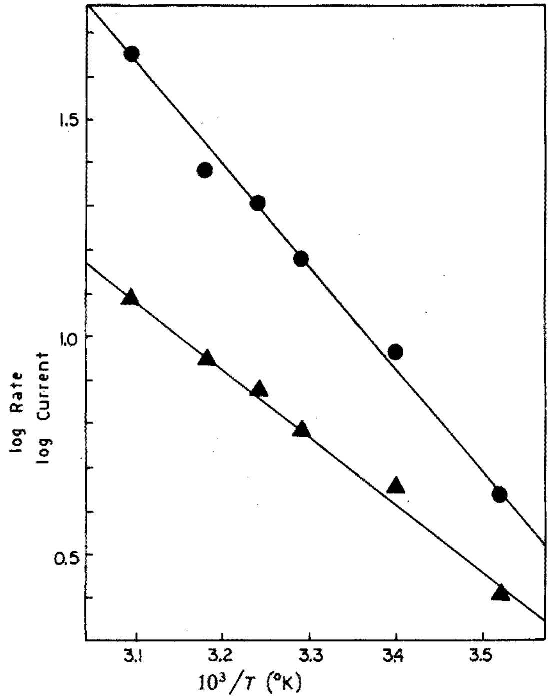

Fig. 6. Effect of temperature on glucose electrode response. ● = Reaction rate method (axis, log rate); ▲ = steady-state current method (axis, log current).

Effect of temperature

The effect of temperature on electrode response was studied from 10° to 50°. The solutions used were 25 ml of glucose solution (1.0 mg ml^{-1}) in quiescent phosphate buffer pH 6.6. Results are shown in Fig. 6. Both methods give linear log response *vs.* $1/T$ (°K) plots. The increase in the steady-state value with temperature follows the general relationship given by Van 't Hoff,

$$\ln K = \ln C - (\Delta H/RT) \tag{9}$$

where R is the gas constant, T is temperature (°K), C is an integration constant, K is the equilibrium constant and ΔH is the heat of reaction. Similarly, the increase in rate with temperature follows the relationship given by Arrhenius,

$$\ln k = \ln A - (E_a/RT) \tag{10}$$

where k is now the rate constant, A a constant, and E_a the activation energy.

Usually an increase in temperature has two effects on enzyme reactions. There is first an increase in the rate with temperature until a maximal rate is achieved, and then a sharply decreasing rate at higher temperatures owing to interconversion of native and denatured forms of the enzyme. The linear plots in Fig. 6 indicate that the major portion of the glucose oxidase is still in its native form at 50°.

Because the response is dependent on temperature, all work was done in a thermostated bath at 30±0.1°. The sensitivity may be increased, if necessary, by going to higher temperatures, but the long-term stability of enzymes decreases as the temperature increases, and other problems such as sample evaporation occur at high temperatures.

Effect of pH

The effect of pH on the response was studied from pH 5.8–7.8 for 5.0 mg of glucose in 5 ml phosphate buffer. Results are shown in Fig. 7. The optimal pH is 6.6 for the rate method and 6.9 for the steady-state method. Others[29,30] have studied the pH dependence of solubilized glucose oxidase reactions and found a broad range of pH 4–7 with a maximum around pH 5.5. There is thus a shift toward more alkaline pH values of 1–1.5 pH units. This result is not at all unexpected. The pH–activity profiles of the polyanionic derivatives of several enzymes have been seen to exhibit this effect[31,32] at low ionic strengths. The local pH within a polycationic derivative will be higher than that in the external solution. These shifts are probably due to the increase in negative charge on the protein. In the case of polyanionic, water-insoluble derivatives in which the enzyme is bound to carboxylic polymers by means of amide linkage, the acylation of amino groups increases the net negative charge on the protein and thus increases the pK_a values of the active-site histidines. In the case of neutral, water-insoluble derivatives in which the enzyme is bound to a polydiazonium salt through its aromatic amino acid residues, the net negative charge on the protein is increased by the coupling to the basic lysyl-ε-amino groups and guanido groups of arginine, and by the acid-strengthening effect of the azo bond on the pK_a of hydroxyl tyrosyl residues[33]. A quantitative discussion of such pH effects has been given by Goldstein and Katchalski[34].

Application to blood glucose determinations

The standard curves for the determination of glucose in blood by the enzyme

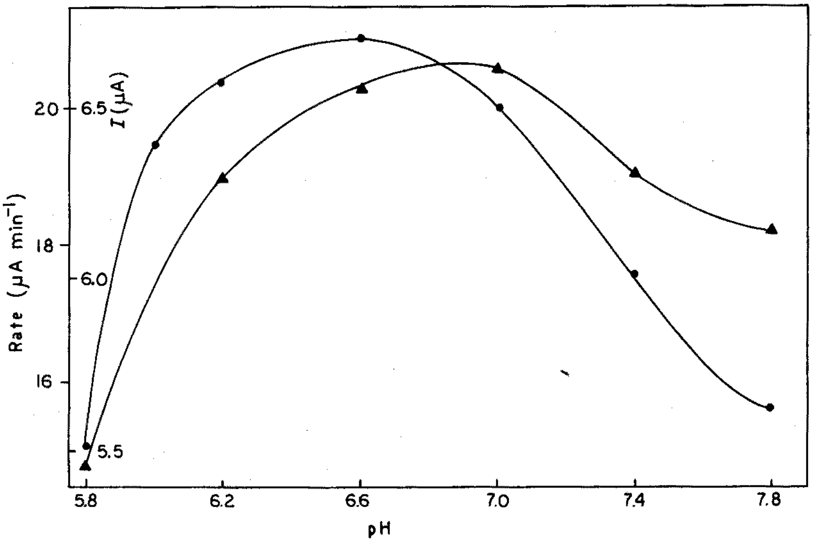

Fig. 7. Effect of pH on glucose electrode response. ● = Reaction rate method (rate axis (μA min^{-1})); ▲ = steady-state current method (current axis (μA)).

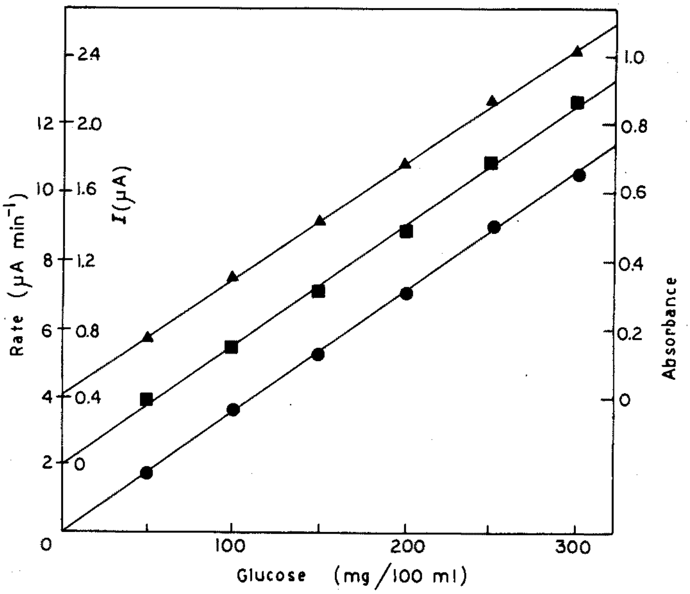

Fig. 8. Calibration curves for the measurement of glucose in 0.1 ml of blood sample. ● = Reaction rate method (rate axis); ■ = steady-state current method (current axis); ▲ = *o*-toluidine method (absorbance axis).

electrode reaction rate, the enzyme electrode steady-state current at 1 min and the *o*-toluidine procedures are shown in Fig. 8. The *o*-toluidine method obeyed Beer's law up to 300 mg of glucose/100 ml. The two enzyme electrode methods were also linear in this region. Linear least-squares analyses of these curves gave lines that passed through the origin (within error) and average relative errors of 1.4%, 2.3%, and 0.9% for the rate, steady-state, and *o*-toluidine methods, respectively. If a differential method of measurement were used for the steady-state method, it is expected that the error would approach that of the other two methods.

The three methods were compared by using sets of eleven samples from the same AQC control. The results are listed in Table II. Figure 9 is a graphical illustration of the correlation between the enzyme electrode rate method and the *o*-toluidine method. All points lie close to the ideal 45° line (solid line) running through the origin. The linear least-squares line is shown as the dashed line. The plots for the other correlations are similar. Correlation coefficients were calculated by the Pearson (product-moment) method. The concentrations of glucose for the eleven samples used in calculating the correlation coefficients with the Nelson–Somogyi and Folin–Wu methods were the assay values given in the AQC set. In every case the correlation between methods was 0.998 or 0.999.

The precision of the enzyme electrode methods was investigated by independently analyzing twenty times a reconstituted freeze-dried control prepared from human blood (Moni-Trol II). The results are shown in Table III. The mean value, 205 mg/100 ml, standard deviation, 3.6, and coefficient of variation, 1.7%, were the same for both methods. The magnitude of the coefficient of variation is similar to that of the percentage relative errors found for the calibration curves

TABLE II

RESULTS OF ANALYSIS OF 11 CONTROL SAMPLES FOR GLUCOSE

Method / Control no.	Glucose (mg/100 ml)		
	o-Toluidine	*Enzyme electrode*	
		Steady-state	*Rate*
1	96	99	100
2	111	116	116
3	126	129	130
4	143	145	145
5	161	161	162
6	176	177	176
7	195	197	196
8	210	214	208
9	231	233	233
10	248	246	253
11	262	266	266

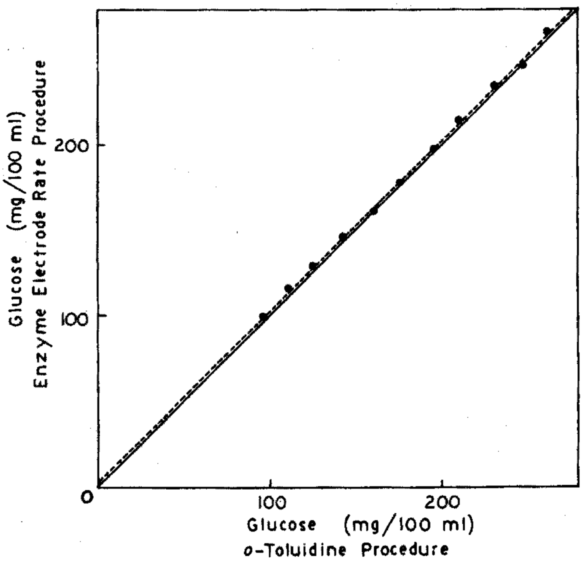

Fig. 9. Correlation curve for the comparison of the *o*-toluidine and enzyme electrode rate procedures. ——, Theoretical 45° line; - - - - - -, least-squares calculated line.

earlier. The reproducibility thus seems limited only by sample manipulation and detecting instrumentation. This precision is similar to that found by Dubowski for the *o*-toluidine method[35].

Interferences and specificity

The number of interferences of this method is considerably less than those of the classical methods that do not incorporate an enzyme in the system. The

TABLE III

RESULTS OF 20 CONSECUTIVE ANALYSES OF A HUMAN BLOOD CONTROL FOR GLUCOSE BY THE ENZYME ELECTRODE METHODS

	Glucose (mg/100 ml)	
	Rate method	*Steady-state method*
Mean result	205.3	205.6
s^a	3.58	3.55
Coefficient of variation[b]	1.74%	1.73%

[a] $s = \{\Sigma d^2/(N-1)\}^{\frac{1}{2}}$.

[b] s/Mean · 100.

selectivity of the glucose oxidase reaction was studied by Gibson *et al.*[36] and Keilin and Hartree[37]. Relative to a rate of oxidation of 100 for β-D-glucose, 2-deoxy-D-glucose gives a rate of only 25. Of the eight aldo-D-hexoses, only D-mannose, D-altrose, and D-galactose are oxidized, and these at extremely low rates. Any alteration in the β-D-glucose molecule tremendously reduces the rate of oxidation. The enzyme is inhibited by Ag^+, Hg^{2+}, Cu^{2+}, *p*-chloromercuribenzoate, and phenylmercury(II) acetate[38]. FAD binding is inhibited with decreasing effectiveness by ADP, ADP-ribose, NAD, ATP, AMP, and adenosine[39]. Most methods using glucose oxidase also require the enzyme peroxidase in their reaction steps. These methods would also be inhibited by species that inhibit the peroxide–peroxidase system. The fact that this method does not require peroxidase is a great advantage over those that do.

Long-term stability

The long-term stabilities of the Type 1, 2, and 3 electrodes were studied by testing the response of each type of electrode to $5 \cdot 10^{-3}$ *M* glucose in phosphate buffer, pH 6.6 at least once a week for several months. When not in use the electrodes were stored in phosphate buffer, pH 6.6, at ambient temperatures (*ca.* 25°). The results are shown in Figs. 10 and 11 for the rate and steady-state methods, respectively. As expected, the long-term stability decreases in the order: chemically bound > physically bound > solubilized. It should be noted here that not only does the Type 3 electrode response decrease drastically with time, it also decreases with each determination of glucose. This is a serious problem and as a result the Type 3 electrode is of little or no use analytically, unless the enzyme layer is changed often. This problem is not encountered with the Type 1 and 2 electrodes consisting of insolubilized enzyme. The curves for the Type 1 and 2 electrodes have a maximum at 20–40 days. In these electrodes the response increases for 20–40 days before beginning to decrease. The decrease in response is due to the decrease in activity of the enzyme layer because of slow denaturation and possibly also slow irreversible inhibition. It is not fully understood why the activity should increase. It may be due to the establishment of diffusion channels in the matrix over a period of time with the concomitant increase in apparent activity until the channel formation ceases and only the denaturation is observed. Or it may be due to the changes in the

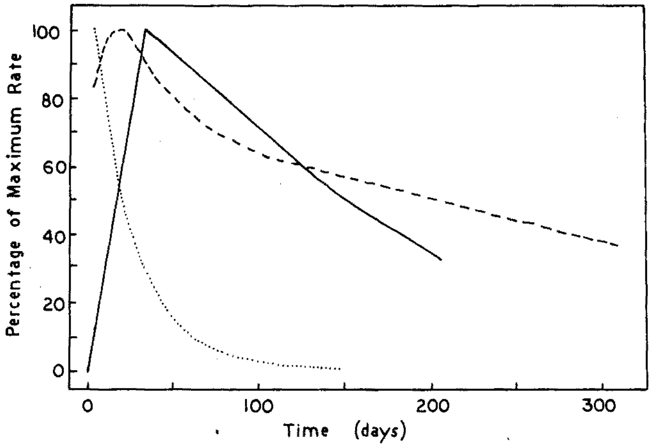

Fig. 10. Long-term stability of glucose electrodes by the rate method. ------, Type 1 electrode; ——, Type 2 electrode; · · · · · ·, Type 3 electrode.

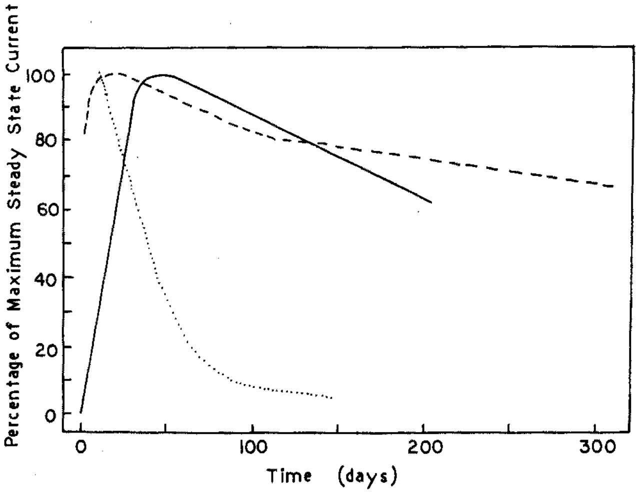

Fig. 11. Long-term stability of glucose electrodes by the steady-state method. -------, Type 1 electrode; ——, Type 2 electrode; · · · · · · ·, Type 3 electrode.

conformation of the fraction of enzyme immobilized in a non-active conformation to the more stable and preferred active conformation. Immobilization in an unfavorable conformation may be due to pH, temperature, or stirring effects during the immobilization process.

The rates of change of response (% of maximum value/day) in the linear regions of the long-term stability curves were calculated by linear least-squares analysis of these regions and are given in Table IV. The average relative percent error of the analysis was *ca.* 2%. The Type 1 and 2 electrodes eventually reach a stability change of −0.12 and −0.32% of maximum response per day by the rate method and −0.08 and −0.25% of maximum response per day by the steady-state method. It was expected that the steady-state method would give a better stability curve,

TABLE IV

RATE OF CHANGE OF RESPONSE FOR LINEAR REGIONS OF STABILITY CURVE

Method	*Electrode type*	*Stability (% change from maximum/day)*		
		Increasing activity	*Decreasing activity*	
Rate	3	None	−3.2	—[a]
Steady-state	3	None	−2.1	—[a]
Rate	2	2.9	−0.43	−0.32
Steady-state	2	2.8	−0.25	—[c]
Rate	1	1.4[b]	−0.68[b]	−0.12
Steady-state	1	1.4[b]	−0.25	−0.08

[a] Response already decayed to low value.
[b] Very short linear range (few days).
[c] Not observed.

because a true steady-state current is essentially independent of the activity of the enzyme. Because a pseudo steady-state method was used with measurement at 1 min, there is some dependence of the response on the activity of the enzyme.

Conclusion

Glucose electrodes have been developed by the coupling of insolubilized glucose oxidase to an electrochemical sensor. They have good accuracy, precision, sensitivity, and selectivity with respect to the measurement of glucose in 0.1-ml blood samples The method is also simple, rapid, and economically feasible for use in physicians' offices, small clinical laboratories or hospitals when rapid measurements are required. The only reagent required is a phosphate buffer solution.

The financial assistance of the National Institutes of Health (Grant No. 5-RO1-GM-17268-03) is gratefully acknowledged.

SUMMARY

An amperometric method utilizing a glucose electrode has been developed for the determination of blood glucose. The time of measurement is less than 12 s if a kinetic method is used and 1 min if a steady-state method is used. The long-term stability of the electrode is *ca.* 0.1% change from maximum response per day when stored at room temperature for over 10 months. The enzyme electrode determination of blood sugar compares favorably with commonly used methods with respect to accuracy, precision, and stability. The only reagent required for blood sugar determinations is a buffer solution. The electrode consists of a metallic sensing layer covered by a thin film of immobilized glucose oxidase held in place by means of cellophane. When poised at the correct potential, the current produced is proportional to the glucose concentration.

RÉSUMÉ

Une méthode ampérométrique est proposée pour le dosage du glucose dans le sang, à l'aide d'une électrode au glucose. La durée d'une mesure est de 1 min ou inférieure à 12 s dans le cas d'une détermination cinétique. En ce qui concerne la stabilité à long terme de l'électrode, la variation maximum de réponse est de 0.1% par jour. Les résultats obtenus correspondent parfaitement bien à ceux trouvés avec les méthodes usuelles.

ZUSAMMENFASSUNG

Für die Bestimmung von Blut-Glukose wurde eine amperometrische Methode unter Verwendung einer Glukose-Elektrode entwickelt. Die Messzeit ist kürzer als 12 s bei Anwendung einer kinetischen Methode und 1 min bei Anwendung einer stationären Methode. Die Langzeit-Stabilität der Elektrode beträgt *ca.* 0.1% Änderung der maximalen Anzeige pro Tag, wenn sie über 10 Monate bei Raumtemperatur aufbewahrt wird. Der Vergleich der Enzymelektrode mit herkömmlichen Methoden zur Bestimmung von Blutzucker fällt hinsichtlich Genauigkeit, Reproduzierbarkeit und Beständigkeit günstig aus. Das einzige für die Blutzuckerbestimmungen notwendige Reagenz ist eine Pufferlösung. Die Elektrode besteht aus einer metallischen Schicht, auf der ein dünner Film von Glukoseoxidase mittels Cellophan festgehalten wird. Bei Vorliegen des Gleichgewichtspotentials ist der hervorgerufene Strom der Glukosekonzentration proportional.

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THE DETERMINATION OF TRACE AMOUNTS OF ZINC, CADMIUM, LEAD AND COPPER IN AIRBORNE PARTICULATE MATTER BY ANODIC STRIPPING VOLTAMMETRY

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Determination of trace elements in airborne particulate matter is very important in air pollution studies. The elemental composition of particles as a function of size may provide a valuable fingerprint for emission source identification. Because the sample is small (5 mg or less) the need for sensitive and accurate methods of analysis is very obvious. In order to save both time and sample, it is also advantageous to perform simultaneous determinations of several elements.

Anodic stripping voltammetry has been applied to the determination of trace elements in the range of 10^{-8}–10^{-10} M[1–5], and has also been used successfully in complex media such as brines[6], sea water[7] and fresh water[8], and in some cases this method found limited use in analysis of particulate matter[9]. Although the principles of the method are very well known, detailed information about the application of this method in trace analysis of airborne particulate matter is not available in the literature. The analytical matrix of the airborne particulate matter is complex and some additional complications are introduced during sample collection and preparation.

In this paper, detailed information about the application of anodic stripping voltammetry for the determination of trace amounts of zinc, cadmium, lead and copper in airborne particulate matter in both conventional and size distribution studies is given. The procedure is also applicable to bismuth. The destruction of the organic collection filter and sample is achieved by a low-temperature ashing process. Possible losses of trace elements because of the reduced operating pressure (0.1 mm Hg) of the low-temperature asher have been investigated and some precautionary measures are given. The sensitivity for each element has been determined and a comparison of results with those obtained by atomic absorption is presented.

EXPERIMENTAL

Instruments and apparatus

A Princeton Applied Research (PAR) M-174 polarographic analyzer connected with a Hewlett-Packard 7005A X-Y recorder, was used throughout this study. The design of a new polarographic cell was required to facilitate the analysis of small volumes of solution while allowing reproducible placement of electrodes and stirring mechanisms. Small volumes are very desirable because the sensitivity of the method

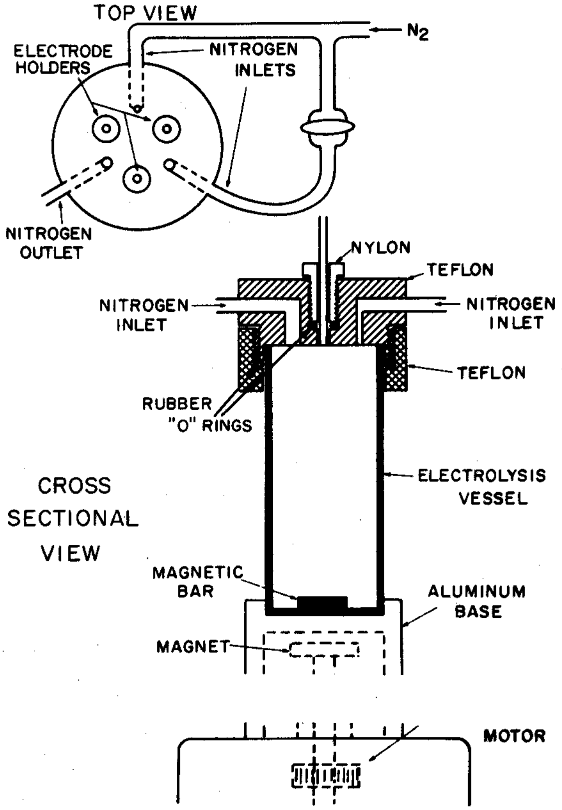

Fig. 1. Diagram of electrolysis cell used for anodic stripping analysis.

decreases with the dilution of the sample. In the case, however, of the hanging mercury drop electrode the volume of the solution must not be reduced below 10 ml because this might affect the linearity of the peak current concentration[10]. All these considerations led to the design of cell which is illustrated in Fig. 1.

The head of the cell was made from Teflon. The nitrogen inlets and outlet, for space economy reasons, were placed on the side of the head, and the gas was carried through or over the solution by means of proper channels. A piece of Teflon tubing, 2 mm O.D., connected with one of the nitrogen inlets was used to deaerate the solution. The other inlet was used for flushing nitrogen over the solution and was connected with a short piece of glass tubing, 5 mm O.D. The deaeration inlet was connected directly to the nitrogen stream, and a stopcock was placed between the flushing over inlet and the nitrogen stream (top view, Fig. 1). The nitrogen was switched from bubbling to blanketing the solution by opening this stopcock. The pressure drop across the small diameter Teflon tubing did not allow the flow of nitrogen through the solution when the stopcock was open. The glass inlets and outlet and the Teflon tubing were secured on the Teflon head by epoxy (Chemgrip made by Chemplast, Inc.).

The electrodes and the solution vessel were sealed using rubber O-rings (Fig. 1). A microburet Brinkmann Instruments Model E-410 hanging mercury drop electrode

(H.M.D.E.) was used as working electrode. A saturated calomel electrode (S.C.E.) was used as the reference electrode. This was separated from the sample solution by a saturated potassium chloride bridge with a fritted glass disc. A helix of platinum wire attached to a 5-mm O.D. glass tubing was used as the counter electrode. All the glass parts coming in contact with the solution were coated with silicone (Siliclad, Clay Adams Co.) to minimize adsorption at the glass surface. Reproducible stirring of the solution was obtained by means of a 600 rev. $\min^{-1}$ synchronous magnetic rotor. A 17 mm long and 3 mm thick magnetic bar, coated with Teflon, was used to stir the solution.

Oxygen impurity contained in the nitrogen used for deaeration was eliminated by means of a catalytic column operated at room temperature. A copper–nickel catalyst (BASF Catalyst R3-11, BASF Colors and Chemicals Inc.) activated with hydrogen was used for this purpose.

Reagents and materials

All the reagents used were analytically pure products (A.R.). Further purification of electrolytes was obtained either by dithizone extraction[10] or electrolytically[11]. A 0.1 *M* potassium nitrate solution was generally used as supporting electrolyte. Ultra-pure acids (Suprapure, Merck) were used for acid dissolution of the sample. Particulate matter was collected on Millipore filters (Celotate) which were impregnated with a 0.1 *M* potassium sulfate solution before ashing.

Procedure

Collect the particulate matter on Millipore filters by using filtration pumps (Bendix 25004 Air Sampling Kit). Cut the filters into *ca.* 1-cm squares and place in special Teflon cups (28 mm O.D., 16 mm height). Wet each filter with 0.2 ml of 0.1 *M* potassium sulfate and ash in a high-vacuum (0.1–0.3 mm Hg) low temperature asher (LFE Corp., Trapelo Div.). This process requires about 2 h at about 30 W of r.f. power. Change of the discharge color from blue to pink indicates the completion of the ashing process.

After ashing, add 2.0 ml of concentrated nitric acid to the Teflon cup to dissolve the residue. Place the cup in a Teflon bomb (using Teflon-coated tweezers), and add 2.0 ml of concentrated hydrofluoric acid. Seal the bomb (Parr Instrument Co.) in the stainless-steel jacket and heat for about 1 h at 120°. After bringing to room temperature, open the bomb and transfer the solution to a 50-ml Teflon beaker. Wash the Teflon cup and bomb three times with 5-ml aliquots of water, transferring the washings to the beaker. Evaporate the resulting solution to about 1 ml, transfer the solution to a 2.0-ml volumetric flask and make up to volume with distilled water. (Samples from the cascade impactor should be evaporated to dryness and then dissolved directly in 15.0 ml of 0.1 *M* potassium nitrate and analyzed.)

Place an aliquot of the solution (usually 0.10 or 0.20 ml) in a Teflon beaker and evaporate again to dryness. Dissolve the residue in 15.0 ml of 0.1 *M* potassium nitrate and transfer to the polarographic cell. Deaerate the solution for 5 min, and then start the magnetic stirrer. Form a mercury drop (diameter about 0.83 mm), with care taken to insure that no air bubbles have formed on the tip of the capillary mercury electrode and then carry out the analysis. Electrolyze the solution at -1.2 V for 3 min; after a 90-s delay (10 s without electrolysis and 80 s with electrolysis), scan from -1.2 V to about $+0.1$ V *versus* S.C.E. at a rate of 5 mV s^{-1}. Repeat the stripping analysis three or four times, under exactly the same conditions, with a fresh drop of mercury every time. Use the average peak current as a measure of the concentration (Fig. 2). This procedure permits the determination of zinc, cadmium, copper and lead concentration in the sample.

Analysis of synthetic samples

Synthetic solutions of similar composition to that of the particulate matter (Table I) were used to evaluate the applicability of the method. The samples were treated as described in the procedure. Figure 2 shows a typical stripping current–

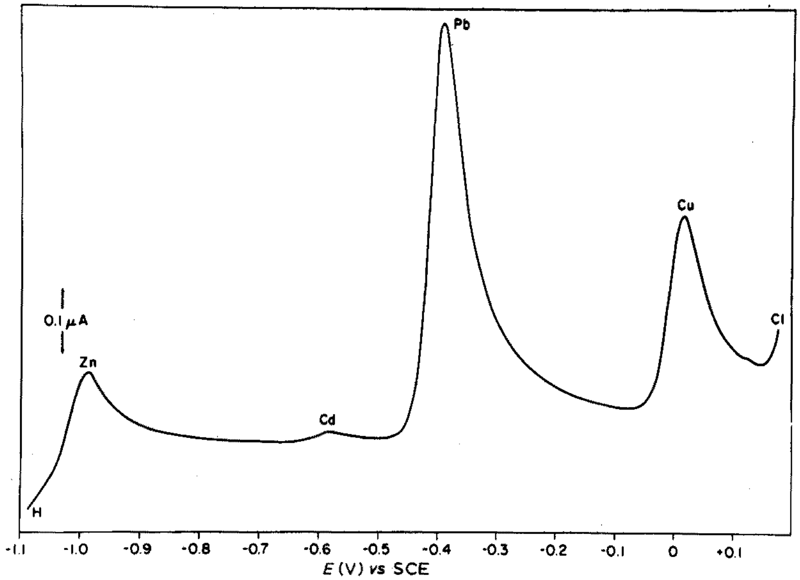

Fig. 2. Typical current voltage curve of a sample in 0.1 *M* KNO_3.

TABLE I

COMPOSITION OF THE SYNTHETIC STOCK SOLUTION[a]

Element	*Concentration (p.p.m.)*	*Element*	*Concentration (p.p.m.)*	*Element*	*Concentration (p.p.m.)*
Al	100.0	Cs	0.02	Ni	0.2
Ba	0.8	Cu	2.0	Pb	10.0
Be	0.02	Fe	60.0	Rb	0.04
Bi	1.0	K	80.0	Sr	0.8
Ca	40.0	Li	0.1	Ti	8.0
Cd	0.2	Mg	20	V	2.0
Co	0.06	Mn	0.9	Zn	2.0
Cr	0.04	Na	20.0		

[a] This solution approximates the relative metal concentrations (with the exception of Si) one finds upon dissolution of particulate matter collected from the Tucson atmosphere.

voltage curve. The method was tested for linearity of the peak currents with the electrolysis times and concentrations. It was found that for electrolysis times up to 10 min, the peak height increased linearly with the time, and for concentrations up to 10^{-7} M increased linearly with the concentration. The sensitivity in stripping analysis is defined as the amount of current per min per mole and usually is given by the expression

$$S = (i_p/tc) \cdot 10^{-5}$$

where i_p is the peak current in mA, t the time of electrolysis in min and c the concentration in mole l^{-1}. The sensitivity of the four elements determined by this method is given in Table II; the precision of this method for synthetic solutions for the four elements is also given. Stripping analysis of the supporting electrolyte, under identical conditions with those of the sample, did not show any significant contamination by these elements. It was found, however, that in the case of zinc and copper there was a significant blank which should be taken into account, especially at very small concentrations. These high blanks for zinc are primarily due to the hydrogen current and the copper blank results from the reaction of chlorides with the mercury of the working electrode. The size of these blanks for zinc and copper was about $2 \cdot 10^{-2}$ and $0.5 \cdot 10^{-2}$ μA, respectively.

TABLE II

SENSITIVITY AND % PRECISION OF ANODIC STRIPPING VOLTAMMETRY FOR SYNTHETIC SOLUTIONS

Element	*Concentration range (μg/15 ml)*	*$S = i_p/tc \cdot 10^{-5}$*	*S (μg)*[a]	*Relative % precision*[b]
Zn	0.1–0.5	$0.9 \cdot 10^{-3}$	0.04	3.0
Cd	0.01–0.05	$1.7 \cdot 10^{-3}$	0.01	3.5
Pb	0.5–2.5	$1.8 \cdot 10^{-3}$	0.05	2.0
Cu	0.1–0.5	$1.3 \cdot 10^{-3}$	0.04	2.5

[a] Practical sensitivity for the given experimental conditions.

[b] Based on the mean of four values obtained on three separate samples.

TABLE III

DETERMINATION OF Zn, Cd, Pb AND Cu BY ATOMIC ABSORPTION (AA) AND BY ANODIC STRIPPING VOLTAMMETRY (ASV) IN AIRBORNE PARTICULATE MATTER

Sample no.	*Zn (μg m^{-3})*		*Cd (μg m^{-3})*		*Pb (μg m^{-3})*		*Cu (μg m^{-3})*	
	ASV	*AA*	*ASV*	*AA*	*ASV*	*AA*	*ASV*	*AA*
1	0.093	0.130	0.015	0.018	1.15	1.17	0.079	0.093
2	0.028	0.038	0.001	0.002	0.102	0.101	0.023	0.027
3	0.023	0.041	0.003	0.002	0.110	0.110	0.027	0.032
4	0.058	0.054	0.003	0.002	0.082	0.083	0.018	0.022
5	0.036	—	0.003	0.003	0.119	0.111	0.021	0.031
6	0.020	0.049	0.002	0.003	0.163	0.171	0.022	0.032

Analysis of particulate matter

One quarter of a Millipore filter was ashed and brought into solution (2.0 ml) as described above. An aliquot (0.10 ml) of this solution was used for stripping analysis. An aliquot (1 ml) of the same solution was diluted to 10.0 ml and analyzed by atomic absorption for the same four elements. Table III gives the results of these determinations; it can be seen that they agree very well. With the exception of zinc, the obtained values are within the expected experimental error. The greater deviation in the case of zinc was expected since at low concentrations the height of the peak was not defined well and the zinc blank was relatively large compared to the sample zinc.

RESULTS AND DISCUSSION

The selection of a suitable sample preparation procedure is extremely important for the analysis of atmospheric particulate matter. It is necessary to select both a usable filtration medium and a dissolution procedure which allows the elements of interest to be dissolved in a matrix suitable for analysis.

In this investigation Millipore filters were chosen as the filter material since these filters have lower trace metal blanks than many other commonly used filters (*e.g.* glass fiber) and because the organic filters could be destroyed before sample dissolution. Complete sample dissolution is required for investigations dealing with the use of elemental ratios as a means of source identification and the chemical characterization of atmospheric particulate matter; this procedure was developed for investigations of this type.

Selection of the ashing procedure for the Millipore filters was also very important. Several ashing techniques were investigated. Wet ashing with sulfuric and nitric acids proved unsatisfactory for stripping analysis for two reasons: first, the resulting solution was very acidic and the necessary neutralization introduced impurities; secondly, the organic matter of the filter did not decompose completely and, therefore, interfered with the stripping analysis. Conventional muffle furnace dry ashing proved to be unsuitable because of the volatility of certain elements such as lead, cadmium and zinc. The low-temperature asher[12] appeared to be the most effective way to ash samples. Under the ashing conditions described here, the Millipore filters were ashed at a temperature of 50–100°. It is known that cadmium sulfate is not volatile and, therefore, conversion in this form should minimize possible losses. For this reason Millipore filters were impregnated with 0.1 *M* potassium sulfate solution, although experiments did not show any significant loss of cadmium during the ashing process (Table IV). It was found, however, that addition of sulfates improved significantly the ashing of the Millipore filters. Without sulfates the ashing was incomplete and the resulting solution usually was yellow and unsuitable for stripping analysis.

The selection of a proper supporting electrolyte is also very vital in stripping analysis. The zinc peak is very close to the hydrogen peak and, therefore, in solution of high acidity the hydrogen peak covers that of the zinc. On the other hand, the matrix of the samples did not allow the use of a phosphate buffer (pH *ca.* 7) because aluminum and iron(III) ions, which were in relatively high concentrations, precipitated, causing coprecipitation and/or adsorption of the four elements under consideration. It was found that potassium nitrate solution was best suited as

TABLE IV

AMOUNT OF CADMIUM RECOVERED BY THE LOW-TEMPERATURE ASHING PROCEDURE

(With and without K_2SO_4 treatment)

μg Cd taken	*μg Cd found*	*% Recovery*
0.143	0.135	94.4
0.143	0.145	101.4
0.143 (K_2SO_4 added)	0.149	104.2
0.143 (K_2SO_4 added)	0.145	101.4

supporting electrolyte, although it does not have any buffering properties. For this reason the acid should be removed completely (incomplete removal of the acid gave inconsistent zinc results) from the sample. This was achieved by double evaporation of the sample to dryness (see *Procedure*).

The actual time for a stripping analysis of particulate matter (excluding ashing, acid digestion and condensation of the sample) was about 1 h, which corresponds to about 15 min for each element. The high sensitivity of the method allowed the use of very small amounts of sample and, most important, stripping analysis is non-destructive. For a similar analysis by atomic absorption, about 10 times more sample is required and the method is destructive. These advantages of stripping analysis make the method very attractive for analysis of particulate matter, especially for size distribution studies of the particulate matter, where the amounts of material sampled are very small (about 0.1–0.3 mg depending on the impactor stage).

This investigation was supported through a grant to the Atmospheric Analysis Laboratory by the Arizona Mining Association.

SUMMARY

The application of anodic stripping voltammetry, with a hanging mercury drop electrode, to the determination of zinc, cadmium, lead and copper in airborne particulate matter collected by filtration is discussed. This procedure allows for the destruction of the filter material followed by the complete dissolution (including silicates) of the collected particulate matter. A low-temperature ashing process is described and the recovery of cadmium in this procedure is studied. Analytical data obtained by anodic stripping and atomic absorption for zinc, cadmium, lead and copper are compared.

RÉSUMÉ

La voltammétrie anodique, avec électrode à goutte pendante de mercure est appliquée au dosage de particules métalliques dans l'air (zinc, cadmium, plomb et cuivre). On procède par filtration, destruction du filtre et dissolution complètes des substances recueillies (y compris les silicates). Un procédé d'incinération à basse température est décrit. Les résultats sont comparés avec ceux obtenus par absorption atomique.

ZUSAMMENFASSUNG

Zink, Cadmium, Blei und Kupfer werden in Proben, die durch Filtration von Luft gesammelt worden sind, durch Voltammetrie mit anodischer Wiederauflösung unter Verwendung einer hängenden Quecksilbertropfenelektrode bestimmt. Bei diesem Verfahren wird das Filtermaterial zerstört und die gesammelte Probe (einschliesslich Silicaten) vollständig aufgelöst. Es wird ein Veraschungsverfahren bei niedriger Temperatur beschrieben und die Erfassung von Cadmium bei diesem Verfahren untersucht. Die analytischen Ergebnisse, die durch anodische Wiederauflösung und durch Atomabsorption für Zink, Cadmium, Blei und Kupfer erhalten worden sind, werden miteinander verglichen.

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SHORT COMMUNICATION

The determination of selenium in sea water by gas chromatography with electron-capture detection

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Selenium is distributed widely in nature with sulfur, but the abundance of selenium is very low compared to that of sulfur. In view of the oxidation–reduction potential, selenium(IV) is the most probable state; selenite and elementary selenium seem to predominate, but selenium(VI) is rarely found in nature. So far as is known, only selenium(IV) occurs in sea water.

Goldschmidt and Strock[1] were the first to determine selenium in sea water; selenium was coprecipitated with iron(III) hydroxide, distilled from hydrobromic acid medium, and determined colorimetrically as elemental selenium. Ishibashi *et al.*[2] used thiourea in a similar procedure. Chau and Riley[3] separated the selenium from iron by ion-exchange and used a spectrophotometric determination with 3,3′-diaminobenzidine; the data obtained were corrected for loss of selenium by applying isotope dilution. Schutz and Turekian[4,5] determined selenium in surface and deep ocean waters by neutron activation.

Recently, a very sensitive method has been proposed for selenium in pure sulfuric acid[6] or tellurium[7]; a gas chromatograph with an electron-capture detector is used, and 4-nitro-*o*-phenylenediamine serves as reagent. The present communication describes the direct gas-chromatographic determination of selenium in sea water without preconcentration. As even about 0.002 μg of selenium in 1 ml of organic extract can be detected by this procedure, only 50–100 ml of sea water is needed. In the absence of pretreatment, no loss of selenium occurs. Though there is some uncertainty in the determination, the time required is very short.

Experimental

Reagents. 4-Nitro-o-phenylenediamine hydrochloride solution. Dissolve 1 g of the reagent in 100 ml of 1 *M* hydrochloric acid. Transfer this solution to a 150-ml separatory funnel and extract the soluble material with 30 ml of toluene by shaking for 5 min. Repeat the extraction twice and store the aqueous phase in a polyethylene vessel. The solution is sufficiently stable to be used for 5 days if stored at room temperature.

Stock selenium(IV) solution. Dissolve 351.3 mg of selenium dioxide in 250 ml of distilled water (1 mg Se ml^{-1}). Prepare working solutions by dilution.

Apparatus. A Shimadzu Model GC-3AE gas chromatograph equipped with an electron-capture detector was used. The glass column (1 m long, 4 mm bore) was packed with 15% SE-30 on 60–80 mesh Chromosorb W. The column and the detector were held at 200°. The nitrogen flow-rate was 53 ml min^{-1}. A Shimadzu Model 250A recorder was used and the chart speed was 5 mm min^{-1}.

General procedure. Put 50–100 ml of sea water and 5 ml of concentrated hydrochloric acid into a 100-ml separatory funnel. Add 2 ml of 1% 4-nitro-*o*-phenylenediamine solution and allow to stand for 2 h. Then, extract the 5-nitropiaselenol formed into 1 ml of toluene by shaking for 5 min and wash the toluene extract with 2 ml of freshly prepared 7.5 *M* hydrochloric acid. Inject 5 μl of the toluene extract into the chromatograph and measure the peak height.

Sea water samples. Filter a sea water sample through a membrane filter (pore size 0.45 μm). Shake 500 ml of the sample vigorously with 100 ml of toluene, to extract toluene-soluble material, before proceeding as above. This washing causes no loss of selenium; if it is omitted, a large error is obtained by an overlapping unknown peak.

Results and discussion

Since a considerable time may elapse between the sampling of sea water and the determination of selenium, the effect of time was examined. Selenium in original sea water and in sea water acidified with hydrochloric acid (1 ml l^{-1}) was determined over a period of a week; both samples showed no appreciable loss of selenium up to 4–5 days. The acidified sample, however, showed a clearer gas chromatogram having only a few unknown peaks (Fig. 1).

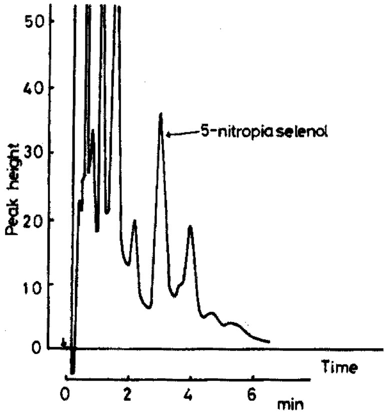

Fig. 1. Gas chromatogram of 5-nitropiaselenol. Column, 15% SE 30/chromosorb W, 4 mm diam. × 1 m glass column; C.G., N_2 (53 ml min^{-1}); temperature, 200°; range, 0.1 V; sample 5 μl (0.02 μg Se in sea water).

Effect of the sea water volume. Toluene (1 ml) was used to extract the 5-nitropiaselenol formed from various volumes of solution (30–130 ml) containing a constant amount (0.02 μg) of selenium. Complete extraction was obtained for up to 100 ml of sample, hence 50–100 ml of sea water was used in further work.

Washing the toluene extract with hydrochloric acid. Because of the high sensitivity of the detector, when the toluene extract was injected directly, an unknown peak overlapped the 5-nitropiaselenol peak even when distilled water was used originally. This peak was easily removed by washing with hydrochloric acid solution. Tests with distilled water alone and water containing 0.02 μg of selenium in the above procedure showed that the unknown substance was removed, without any back-extraction of 5-nitropiaselenol, when the toluene extract was washed with 2 ml of freshly prepared 6–7.5 *M* hydrochloric acid solution.

Selenium(VI) in sea water. So far as is known, no selenium(VI) is found in sea water, and this is supported by thermodynamic considerations. The possibility of selenium(VI) was checked as follows.

Sea water (50 ml) and 5 ml of concentrated hydrochloric acid were heated with 5 ml of $3 \cdot 10^{-2}$ *M* titanium(III) chloride on a boiling water bath for 10 min; after cooling, 0.8 ml of 0.1 *M* bromine–bromide redox buffer solution was added and the mixture was left for 1 h. The General procedure was then applied to this solution. An analogous blank determination was carried out on distilled water. It was found that selenium(VI) was absent from sea water within the identification limit of this method (0.02 μg l^{-1} of sea water).

Calibration curve. The calibration curves were prepared from known amounts (0–0.025 μg) of selenium(IV) in distilled water (50 and 100 ml), sea water and artificial sea water. Artificial sea water was prepared by dissolving 14.0 g of NaCl, 6.3 g of $MgCl_2 \cdot 6H_2O$, 2.3 g of Na_2SO_4, 0.9 g of $CaCl_2 \cdot 2H_2O$ and 0.4 g of KCl in 500 ml of water (Kall's artificial sea water). The curves were parallel to each other (Fig. 2). These results also show that the substances contained in sea water do not interfere with the reaction of selenium with 4-nitro-*o*-phenylenediamine.

Determination of selenium in sea water. Selenium in both 50 ml and 100 ml of sea water was determined by the proposed method; 50 ml of sample with 0.02 μg of selenium(IV) added was also used. As 0.02 μg of selenium was always obtained when the former values were subtracted from the latter, this method is proved to be suitable for the determination of selenium in sea water. The results are shown in Table I.

As the sensitivity of an electron-capture detector tends to vary during operation, a series of experiments should be carried out successively and unknown contents of selenium should be determined along with standard samples which contain similar amounts of selenium.

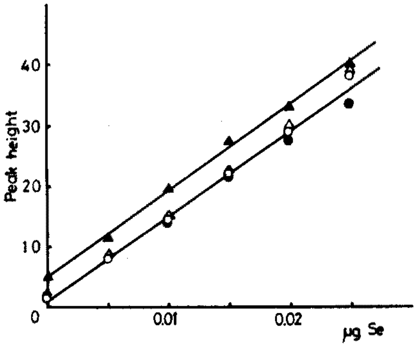

Fig. 2. Calibration curves. (○) 50 ml of distilled water; (●) 100 ml of distilled water; (△) 50 ml of sea water; (▲) 50 ml of artificial sea water.

TABLE I

SELENIUM CONTENT IN SEA WATER

Sample[a]	*Selenium content in sea water*[b] (*$\mu g\ l^{-1}$*)
Seashore, June 14th, 1972	0.04 ± 0.01
Seashore, June 20th, 1972	0.07 ± 0.01
Offshore, July 19th, 1972	0.08 ± 0.01

[a] These were sampled at Shibukawa, Okayama Pref., Japan. Samples contain 1 ml of concentrated hydrochloric acid per liter.

[b] The mean value of four measurements.

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SHORT COMMUNICATION

Determination of nitrate in feedstuffs

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(Received 6th November 1972)

In a search for the best determination of nitrate which would provide a rapid but reliable product control of concentrated feedstuffs of high protein content, several common methods were examined. The results of these tests can be summarized as follows.

Direct potentiometric measurement with a nitrate ion-selective electrode[1–3] is reliable only when interfering chloride ions are eliminated or their concentration is held strictly constant. Polarographic methods[4–7] are not applicable in simple aqueous solutions or in solvent extracts, primarily because polypeptides and peptones influence the catalytic currents on which the measurements are based. Of the many methods based on nitration reactions[8,9], the Herberts–Thijsen modification[10] of the Balks–Reekers method[11] was examined. Contrary to reports in the literature, it was found that chloride interference was within the normal experimental error up to a chloride concentration of 1%. When the plant material was dried mildly at about 60–65°, the colour change from the interfering side-reactions of xylenol was also decreased. The method was also successfully applied to protein concentrates. However, this method has severe disadvantages in that a blank-without-reagent must be done at each step of each measurement, and many extractions with dangerous unpleasant solvents are necessary.

More convenient are those methods in which the nitrates are determined spectrophotometrically as nitrites after diazotation[12–14]. Reproducible results were achieved by the AOAC standard method[15] even with concentrates of high protein content. However, this procedure is also discontinuous and demands much attention. The purpose of the work described here was to overcome these difficulties.

Experimental

Reagents. All chemicals used for the solutions and for the preparation of cadmium grains were of analytical grade.

Apparatus. Absorbance measurements were made with a Zeiss Spekol Spectralcolorimeter.

Voltammetric measurements were done with a Radelkis OH102 Polarograph.

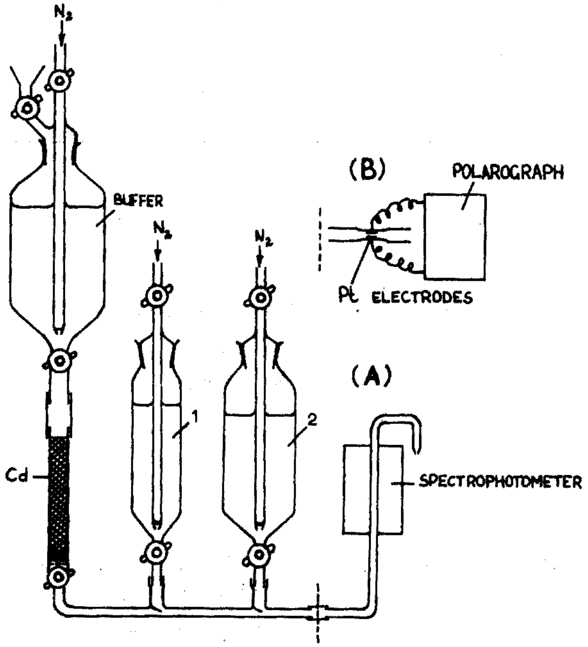
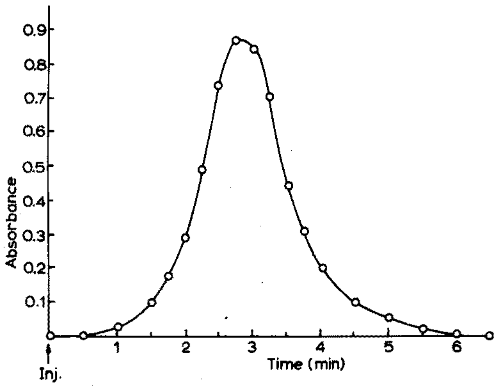


Fig. 1. Schematic diagram of the experimental device for spectrophotometric (A) and biamperometric (B) measurements. Vessel 1, KI + starch. Vessel 2, HCl solution.

Experimental device and procedure. Fig. 1 shows the experimental device which is made of glass. Over the reduction column filled with cadmium grains (20–40 μm diam.) there is a reservoir for the ammonia–ammonium chloride buffer solution of pH 9.6. The first feedtank is filled with a 10% (w/v) potassium iodide solution with or without starch solution and the second one with 2 *M* hydrochloric acid. All three tanks are connected to a nitrogen supply. The flow-rate of the buffer solution and the speed of the continuous feed of the iodide solution and of the acid can be adjusted by altering the gas pressure and by turning the taps, so that the optimal relations of the reactions can be established. A portion (1–2 ml) of solution containing 10–150 μg of nitrate is injected by means of a syringe into the polyethylene connecting tube above the reduction column. The nitrite developed as the solution flows through the column generates iodine from the iodide when it reaches the acidic medium as it moves along the tube. This iodine is measured continuously spectrophotometrically or biamperometrically. In the spectrophotometric method starch solution is fed along with the potassium iodide solution and a simple flowing cuvette of narrowed cross-section is used; absorbances are measured at 580 nm. For biamperometric measurement a simple dead-stop cell is constructed of parallel platinum plates soldered in a glass tube of narrowed cross-section. This bottleneck makes unnecessary the insertion of a stirrer in either case.

All solutions must be cleaned by bubbling with oxygen-free nitrogen before the flow is started, because the reaction is sensitive to oxygen. The flow-rate of the buffer and the solutions to be added must be held strictly constant within a run. The achievement of this constancy with this experimental equipment still calls for care, but by suitable pumping will be realized automatically.



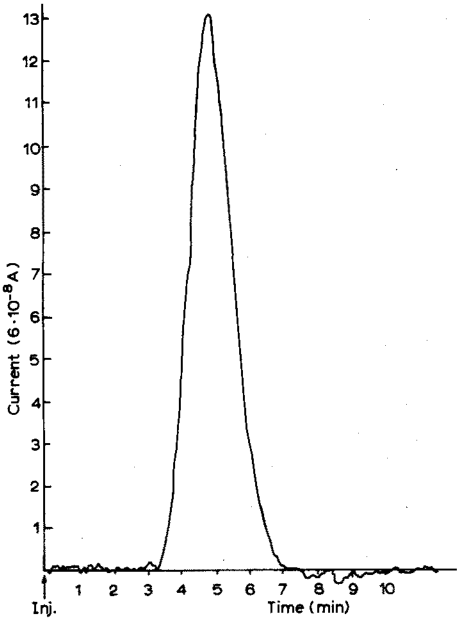


Fig. 2. A typical plot of absorbance data for 100 μg NO_3^-/2 ml.

Fig. 3. A typical diagram of the biamperometric measurement for 100 μg NO_3^-/2 ml.

Analytical application and results

A typical plot of absorbance data against time intervals starting from injection is shown in Fig. 2. The points of the curve were obtained from readings every 30 s. Evaluation of such diagrams by the weighting–integration method proved that the relationship between the integral value and the given nitrate content was linear.

Fig. 3 shows a diagram plotted from biamperometric data; a potential of 0.05 V was switched between the two platinum electrodes and the change of current with time was measured by a polarograph. Again, application of the weighting–integration method showed a linear relationship between the area under the curve and the amount of nitrate injected.

When the flow-rate was increased, the curves became more abrupt and evaluation could be done simply from the peak heights. The sensitivity decreased because the reduction was incomplete, but when the conditions were strictly constant, series measurements could be rapidly performed.

The detection limit of this experimental device was 20 μg of nitrate spectrophotometrically and 10 μg of nitrate biamperometrically. The relative standard deviation was 6.2% for the spectrophotometric method, and 1.4% for the biamperometric method.

When plants and concentrated feed materials are analyzed, the standard solutions must be measured in exactly the same base solution as the injected solution. The nitrate contents of various feed plants and plant protein concentrates by the proposed method and by referee methods are shown in Table I.

TABLE I

SOME EXPERIMENTAL DATA FOR COMPARISON

	% Nitrates/dry material		
	Balk–Reekers method	*A.O.A.C. method*	*Proposed method*
Alfalfa	0.33	0.32	0.37
Alfalfa	0.02	0.06	0.05
Cabbage	1.10	1.08	1.05
Cabbage	0.96	1.05	1.01
Cabbage	0.20	0.17	0.18
Wheat + alfalfa	0.26	0.25	0.25
Wheat + alfalfa	0.19	0.24	0.23
Wheat + alfalfa	0.18	0.17	0.20

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SHORT COMMUNICATION

The determination of diazepam in serum by differential pulse polarography

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Diazepam (7-chloro-1,3-dihydro-1-methyl-5-phenyl-2H-1,4-benzodiazepine-2-one, "Valium", "Vival", "Stesolid") is a psychotherapeutic agent which is extensively used as a tranquillizer. In a previous paper dealing with the polarographic determination of diazepam in pharmaceuticals[1], earlier work was listed; since then, the d.c. polarographic behaviour of the drug has been further investigated[2]. The present communication describes a rapid pulse polarographic method for the determination of small amounts of the drug in serum.

Experimental

Pharmaceutical-grade diazepam (A/S Apothekernes Laboratorium for Specialpræparater, Oslo) was used. Stock solutions were prepared by dissolving the appropriate amount of the drug in 0.1 *M* sulphuric acid. Only freshly prepared stock solutions were used and the solutions were discarded after 1 h.

Polarograms were recorded with a PAR polarographic analyzer, model 174, in the differential pulse mode. An Ag/AgCl/saturated KCl electrode served as reference electrode. All experiments were performed at $25 \pm 0.1°$. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 5 min and passing it over the solution during the electrolysis.

Results

Polarograms of diazepam recorded from 0.1 *M* sulphuric acid exhibit a well-defined 2-electron wave. The d.c. current is diffusion-controlled and increases linearly[1] with the concentration of diazepam in the range 10–200 μg ml^{-1}. Hence, 0.1 *M* sulphuric acid was chosen as supporting electrolyte. Preliminary experiments showed that the most well-defined differential pulse polarograms were obtained with a modulation amplitude of 100 mV, scan rate 5 mV sec^{-1} and a drop time of 1 s.

Polarograms recorded from 0.1 *M* sulphuric acid with various amounts of diazepam present showed that the peak current increased linearly with the bulk concentration of the drug and that concentrations of diazepam down to 0.03 μg ml^{-1} could easily be determined by pulse polarography. The peak potential of diazepam recorded from 0.1 *M* sulphuric acid was -0.61 V *vs.* Ag/AgCl and -0.98 V *vs.* a mercury pool.

Direct polarographic determination of diazepam in sera was not possible because the wave was greatly distorted by the adsorbed film of surface-active proteins on the electrode surface. Consequently, diazepam had to be separated from the proteins before the determination. Ethyl ether (see, *e.g.* Tomsett[3]) and petroleum spirit[2] have previously been recommended for extraction of diazepam from sera. Recently, Berlin *et al.*[4] found that benzene is a more effective extractant; if the serum sample is mixed with an equal volume of saturated potassium chloride there is a 100% distribution of diazepam into the benzene phase in a single extraction[4]. Hence, benzene was chosen as extraction agent.

In a series of experiments in which various amounts of diazepam were added to 5-ml samples of horse serum, the solution was mixed with 5 ml of saturated potassium chloride and the drug was extracted with 30 ml of benzene; it was verified that 100% of the diazepam was extracted into the organic phase. The amount of diazepam in the benzene phase was easily determined by evaporating the solution to dryness in a Buchi Rotavapor, dissolving the residue in 0.1 *M* sulphuric acid and recording the polarogram.

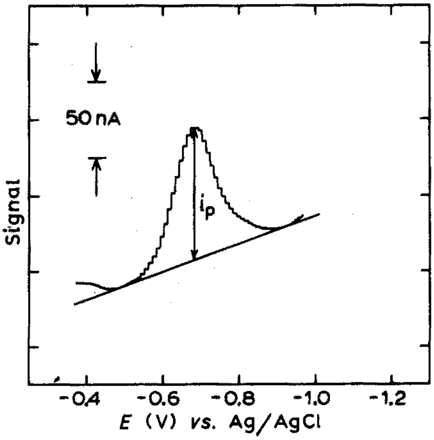

Fig. 1. Differential pulse polarogram of 0.114 μg of diazepam per ml after extraction of the drug from serum with benzene, evaporation to dryness and dissolution of the residue in 0.1 *M* sulphuric acid.

Polarograms of diazepam in sulphuric acid after extraction of the drug from serum with benzene were very well defined (Fig. 1). However, the peak height was less than that of the same amount of the drug in pure sulphuric acid. This was probably due to co-extraction of surface-active materials from the serum, which made the electrode reaction more irreversible. However, the data were perfectly reproducible and the measured peak height increased linearly with the concentration of diazepam in the serum sample over the range 0.05–1.0 μg per ml of serum.

In order to achieve a complete separation of the aqueous and organic phases after the extraction, the mixture had to be centrifuged. However, it was more convenient to transfer only 80–90% of the clear supernatant benzene phase to the Rotavapor and determine the amount of diazepam from a standard curve prepared by the same procedure.

Based on the above experiments the following procedure is suggested.

Recommended procedure

Transfer 5.00 ml of serum containing 0.05–1.0 μg diazepam per ml to a separatory funnel and add 5 ml of saturated potassium chloride and 30.00 ml of benzene. After extraction for about 15 min, transfer 25.00 ml of the organic phase to a Rotavapor and evaporate to dryness. Dissolve the residue by gentle shaking with 5.00 ml of 0.1 *M* sulphuric acid and transfer the solution to a polarographic cell. Remove dissolved air with purified nitrogen and record the polarogram. Measure the peak height (at −0.6 V *vs.* Ag/AgCl) and determine the amount of diazepam from a standard curve prepared by the same procedure.

If a small "mercury pool" polarographic cell is available, the sample volume can be reduced to 2.00 ml. In that case, add 2 ml of saturated potassium chloride and extract the drug with 10.00 ml of benzene. Dissolve the residue in 2.00 ml of 0.1 *M* sulphuric acid and measure the peak height at −0.98 V *vs.* the mercury pool.

The results of a few determinations of diazepam in serum by the above procedure are given in Table I.

TABLE I

DETERMINATION OF DIAZEPAM IN 5-ml SERUM SAMPLES

Diazepam taken ($\mu g\ ml^{-1}$)	*Current (μA)*	*Diazepam found ($\mu g\ ml^{-1}$)*	*Error (%)*
0.057	0.038	0.061	+7.0
0.096	0.060	0.091	−5.2
0.114	0.080	0.115	+0.9
0.171	0.128	0.170	−0.6
0.228	0.180	0.230	+0.9
0.570	0.460	0.570	0
1.140	0.940	1.135	−0.4
2.280	1.85	2.290	+0.4

Conclusion

The proposed method is very rapid and accurate and it is useful for determination of diazepam in the concentration range 0.05–1.0 μg per ml of serum. The detection limit is 0.01 $\mu g\ ml^{-1}$. The polarographic method is specific for diazepam. No material is extracted from serum that interferes with the reduction of the drug. Moreover, other benzodiazepines (chlordiazepoxide[5] and nitrazepam[6]) which are extracted by the same procedure, are reduced in two steps and the first step occurs at much less negative potentials.

The authors wish to thank cand. pharm. R. Gjermundsen and cand. pharm. V. Holm, Pharmaceutical Research Laboratory, A/S Apothekernes Laboratorium, Oslo, for valuable discussions and for the supply of the drug.

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Analytica Chimica Acta, 64 (1973) 477–480

SHORT COMMUNICATION

A potassium-selective silicone-rubber membrane electrode based on a neutral carrier

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Electrically neutral ion-selective carriers, such as certain antibiotics[1–3], and other neutral organic molecules which form complexes with alkali and alkaline earth metal cations[2,4–6], are attractive components for membrane electrodes of high ion selectivity[2,3]. With such ligands, ion-selective electrodes of analytical significance for potassium[6–10], ammonium[11,12], barium[13], and calcium[14] ions have been prepared. The membranes of these electrodes contain the ion-selective ligand in an adequate solvent on supports such as filter membranes[6,9,13,14], porous cellulose acetate[7], polyvinyl chloride[15], and collodion[8,12 ★].

Because the cross-linked silicone-rubber supports[16] have been very successfully used for heterogeneous precipitate-based ion-selective electrodes[17], the aim of the present contribution was to study whether electrically neutral ligands behave as carriers in such inert matrices.

Experimental

Electrode system. For the e.m.f. measurements cells of the type: Ag:AgCl, 0.01 *M* KCl||membrane||sample solution|0.1 *M* LiCl in agar gel|0.1 *M* LiCl, Ag:AgCl (1); or Ag:AgCl, 0.01 *M* KCl||membrane||sample solution|0.1 *M* NH_4NO_3KCl (Std.), Hg_2Cl_2:Hg (2) were used. The membrane electrode construction (electrode body Philips type IS 560) has been described elsewhere[6].

Preparation of the membranes. The chemical compositions by weight of the membranes are given in Table I.

In the case of the PVC membranes (I, II) the solution of the membrane components in tetrahydrofuran (*ca.* 4 ml) was poured into a glass ring (2.3 cm diam.) in contact with a glass plate and dried during two days at room temperature (see ref. 18).

For the preparation of the SR (III–V) membranes, the mixture of the membrane components was poured on a glass plate and polymerized during 30 min at room temperature (see ref. 16).

★ Although the composition of the membrane is not given in these publications, there is information available that collodion and electrically neutral carrier antibiotics were used.

TABLE I

COMPOSITIONS OF THE MEMBRANES STUDIED (wt.-%)

Components	*Membranes*				
	I	*II*	*III*	*IV*	*V*
Valinomycin	2.5	1.2	4.7	3.3	5.1
PVC[a]	35.0	24.7	—	—	—
SR[b]	—	—	73.5	32.2	92.0
Diphenyl ether	45.0	—	—	—	—
Dibutylsebacate	17.5	—	—	—	—
Phthalic acid dibutyl ester	—	74.1	17.7	—	—
Tetramethoxysilane	—	—	—	61.6	—
Cross-linking agent[c]	—	—	4.1	2.9	2.9

[a] Polyvinyl chloride (SDP hochmolekular, Lonza AG, Basel, Switzerland).
[b] Silopren K1000 (Farbenfabriken Bayer AG, Leverkusen, Germany).
[c] Dibutyltindilaurate/hexamethoxysilane (1/2 wt.).

E.m.f. measurements. All measurements were performed at 25° as described earlier[6]. The standard deviation of a single determination was 0.1 mV.

Reagents. Double-distilled water (from quartz) and chemicals of the highest purity available were used throughout to prepare the solutions. The buffer solutions were obtained by mixing triethanolamine and ethanolamine with acetic acid or hydrochloric acid to a total concentration of amine below 0.1 *M*.

TABLE II

RESPONSE OF DIFFERENT POTASSIUM-SELECTIVE ELECTRODES

Valinomycin containing membrane (see Table I)	*Electrode response*			
	Range[a] ($-\log a_{\mathrm{K}^+}$)	*Slope*[a] ($mV/-\log a_{\mathrm{K}^+}$)	*Reproducibility (95% confidence limit) (mV)*	*Drift* (ΔmV/*time*)
Millipore filter/diphenyl ether[6]	1–5	59	±0.5	< ±1.4 mV/150
	5–6	45		
PVC/diphenyl ether, dibutylsebacate (I)	1–5	57	±2.0	+0.6 mV/24
PVC/phthalic acid, dibutyl ester (II)	1–4	55	±1.0	+4.5 mV/24
	4–5	40		
SR/phthalic acid, dibutyl ester (III)	1–4	55	±0.6	+0.8 mV/24
	4–5	49		
SR/tetramethoxysilane (IV)	1–4	54	>10	+18 mV/24 h
	4–5	35		
SR (V)	1–5	59	±0.5	<0.1 mV/120
	5–6	45		

[a] Activities in mole l^{-1} (*M*).

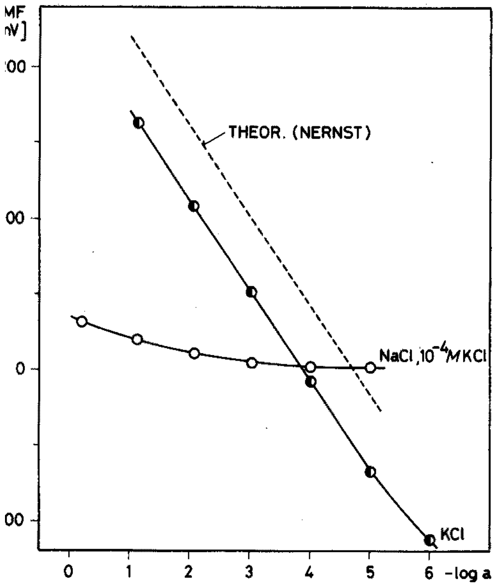
Results and discussion

Some of the results obtained with cell (2) are presented in Table II. The characteristics of the silicone-rubber valinomycin electrode (V) are similar to those observed for the filter membrane electrode described earlier[6]. Although the membrane V contains considerably less than 3% of solvent or softener (see Tables I and II) valinomycin seems to maintain its carrier properties. In contrast to the precipitate-based silicone-rubber electrodes in which the minimum concentration of precipitate in the membrane is 30 wt.-%, it was found that 5 wt.-% of valinomycin was adequate for the preparation of the electrode. It is also of interest that the PVC membranes without softener did not show a potassium ion response at all.

The e.m.f. response of the membrane V in cell 2 is shown in Fig. 1. It is linear in the range 10^{-1}–10^{-5} *M* with a slope of 59.2 mV/$-\log a_{K^+}$ (theoretical value: 59.2). The stability of cell 2 (membrane V) was studied in an aqueous 10^{-2} *M* solution of potassium chloride over a period of 65 h by taking readings at time intervals of 30 min (25.0±0.1°). A drift smaller than 0.1 mV and a standard deviation of a single determination of 0.15 mV were observed. The stability of the electrode potential was ±0.2 mV over a period of 120 h in unthermostatted conditions. When the sample solutions were changed in the 10^{-1}–10^{-3} *M* KCl range, the e.m.f. came within 0.1 mV of the final potential in less than 3 s.

Except for the discrimination against hydrogen (Fig. 2) and cesium ions, the selectivity data determined as described earlier[19] for cell (1) showed good agreement with values obtained for the filter membrane electrode[6] (see Table III).

After 4 weeks of routine use of the electrode (membrane V) in different aqueous solutions, no change whatsoever of the electrode characteristics was found.



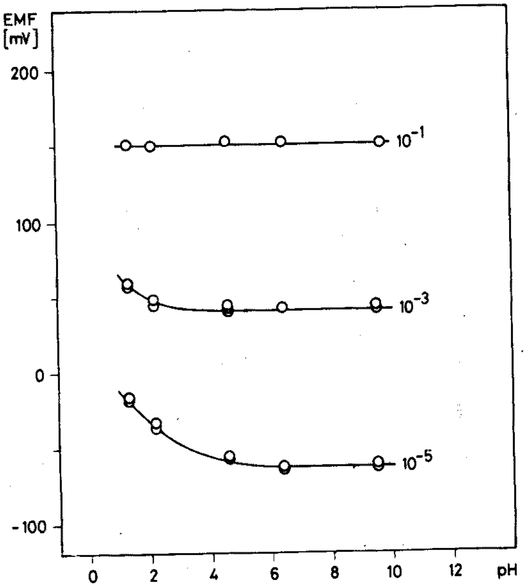


Fig. 1. Response of the silicone rubber membrane electrode with valinomycin as ion-selective component (Cell 2; 25°).

Fig. 2. Steady-state electrode potentials in buffered KCl solutions of the molar concentrations indicated at different pH (Cell 2).

TABLE III

SELECTIVITIES $K^{\mathrm{Pot}}_{\mathrm{KM}}$ OF POTASSIUM ELECTRODES BASED ON VALINOMYCIN

Interfering cation M	*Membrane*	
	SR membrane V	*Millipore filter/ diphenyl ether*[6]
K^+	1	1
H^+	$1.8 \cdot 10^{-3}$	$5.0 \cdot 10^{-5}$
Li^+	$6.3 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
NH_4^+	$2.3 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$
Na^+	$3.3 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
Rb^+	1.9	1.9
Cs^+	$3.4 \cdot 10^{-3}$	$4.0 \cdot 10^{-1}$
Ca^{2+}	$8.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
Sr^{2+}	$5.4 \cdot 10^{-4}$	—
Mg^{2+}	$6.2 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
Ba^{2+}	$7.2 \cdot 10^{-4}$	$6.0 \cdot 10^{-5}$

Conclusion

A new potassium-selective silicone-rubber membrane electrode based on the neutral carrier valinomycin has been developed. The electrode selectivity for most alkali and alkaline earth metal cations is comparable to that of the conventional liquid membrane electrodes. Over a period of 65 h no drift in e.m.f. was observed. The response time usually is less than 3 s.

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Analytica Chimica Acta, 64 (1973) 481–482

ANNOUNCEMENT

Meetings of Gesellschaft Deutscher Chemiker 1973

March	*Division "Photochemistry"* Meeting in Göttingen.
26th–30th March	*Meeting of University Teachers in Chemistry* in Münster.
1st–5th April	*EUCHEM Conference "Solid State Chemistry at High Pressures"* Schloss Elmau/Mittenwald.
2nd–5th April	*Mass Spectrometry Working Party of the Division "Analytical Chemistry"* Spring Meeting of the Section "Atomic and Molecular Collision Processes" in München.
week from 2nd–7th April	*Joint GDCh-Division Meeting in Erlangen-Nürnberg* with the Divisions "Analytical Chemistry", "Nuclear-, Radio- and Radiation Chemistry", "Food and Forensic Chemistry", "Water Chemistry", German Working Group for Spectroscopy.
5th–6th April	*Division "Solid State Chemistry"* Meeting in Lindau.
28th–30th May	*Division "Water Chemistry"* Annual Meeting in Bad Zwischenahn b. Oldenburg.
20th June	*Division "Private Consulting Chemists"* Meeting in Frankfurt (M).
25th June	*GDCh-Chemistry Day with Festive Meeting on the occasion of ACHEMA 1973.*
Summer 1973	*Chromatography Working Party of the Division "Analytical Chemistry"* Discussion in Bochum.
3rd–8th September	*XXIV IUPAC Congress (International Congress of Pure and Applied Chemistry)* in Hamburg Section 1 High Polymers Section 2 Chemistry of Organic Natural Products Section 3 Solid State Chemistry Section 4 Compounds of Non-metals Section 5 Applied Electrochemistry Section 6 Radiochemistry Section 7 Symposium on Information and Communication in Chemistry Symposia: Joint Symposium on Modern Methods for the Treatment of Waste Water in Theory and Practice Joint Symposium on Medicinal Chemistry.

10th–14th September	*Division "Nuclear-, Radio- and Radiation Chemistry" together with Kernforschungsanlage Jülich* 7th International Hot Atom Chemistry Symposium in Jülich.
18th September	*Division "Water Chemistry"* Meeting in Haus der Technik, Essen
26th–28th September	*Division "Food and Forensic Chemistry"* German Food Chemistry Day in Dortmund.
Autumn 1973	*Division "Industrial Juridical Protection"* Meeting in München.
27th–29th September	*Division "Chemical Education"* Annual Meeting in Marburg.
4th–5th October	*Division "Applied Electrochemistry"* Meeting in Ludwigshafen.
9th–13th October	*40th Meeting of GDCh-Division "Pigments and Dyes" together with Deutsche Gesellschaft für Lackforschung e. V.* in Bad Neuenahr.
10th–15th October	*5th European Symposium "Food – Rheology in Food Processing and Food Quality"* in Zürich.
11th–12th October	*Division "History of Chemistry"* Meeting in Frankfurt (M).
3rd–5th December	*Division "Water Chemistry"* Seminar of Technische Akademie in Wuppertal – Chemical, Physical and Biological Methods for Analysis of Water and Waste Water.

Details of the meetings listed above may be obtained on request from Gesellschaft Deutscher Chemiker, D-6000 Frankfurt (M), Germany, Postfach 119075.

Analytica Chimica Acta, 64 (1973) 483–489

BOOK REVIEWS

L. S. Birks, *Electron Probe Microanalysis*, Vol. 17 of Chemical Analysis, Edited by P. J. Elving and I. M. Kolthoff, Wiley–Interscience, New York, 2nd Ed., 1971, xi + 190 pp., price £7.00.

When the first edition of this book was published in 1963 the electron probe microanalyser had just graduated from a very specialised instrument used mainly by metallurgists into a reliable device used for the analysis of a wide range of small samples by an equally wide spectrum of scientists. Nine years later, many further developments have taken place, and electron probe microanalysis has become a valued and well-established technique. These developments are fully described in this second edition, so that the present text is a substantial revision of the previous edition. Like its predecessor, it will provide all users and potential users of electron probe microanalysis with a clear and balanced account of the theory, instrumentation and applications. A final chapter includes brief accounts of related techniques such as scanning electron microscopy, electron spectrometry and the ion probe microanalyser. There are appendices of mass attenuation coefficients for K_α and $L_{\alpha 1}$ lines, fluorescent yields, jump factors, excitation energies, characteristic wavelengths and analyser crystal spacings.

A. Townshend (Birmingham)

M. Kuhnert-Brandstätter, *Thermomicroscopy in the Analysis of Pharmaceuticals*, International Series of Monographs in Analytical Chemistry, Vol. 45, Pergamon Press, Oxford, 1971, x + 409 pp., price £ 10.00.

Reading this volume, the reviewer was irresistibly reminded of the meticulous labours of the famous Dr. Hassall in London during the mid 1860's on the microscopical examination of foods and drugs as a major factor in the determination of their adulteration. Hassall's work at once brought the microscope to the forefront as an analytical tool. By the chronicling of an immense amount of detailed and highly skilled observations on thermomicroscopical phenomana with medicinal chemicals, Professor Kuhnert-Brandstätter has provided further impetus for the use of this valuable instrument. She pays tribute to her mentor Ludwig Kofler and his wife in bringing the potentials of thermomicroscopy to the notice of chemists and pharmacists. How useful are the techniques that have evolved from her partnership with the Koflers is shown by the very large number of precise identifications of drug substances which she shows to be possible with only minute samples.

The book opens with descriptions of the Kofler hot stage, the newer Mettler hot stage, and the Kofler hot bench, which has proved advantageous in identification of labelled substances. The author stresses that the different techniques involved must be learnt—like the pharmacist's "secundum artem"—but that they are not difficult. In the chapters describing these techniques the determination of the melting point and melting range and the influence of such factors as grain size, thermal instability and the production of metastable modifications are treated. Observation and interpretation of the melting behaviour of substances calls for some expertise and experience, but the presence of solvent adducts and polymorphic forms can be readily detected. The refractive index of the melt may be determined, as well as the ultraviolet absorption characteristics. The necessary precautions for the performance and interpretation of mixed melting point tests are outlined.

A fascinating account of investigations to determine enantiotropic and monotropic polymorphism reveals that phenobarbitone has been prepared in eleven modifications. Many sulphonamides also show polymorphism and it is surprising to learn that an appreciable number of commercially available sulphonamides are polymorphic to varying degrees. Bioavailability studies on pharmaceutical formulations containing these and other polymorphic medicinals might produce some interesting findings. Much very valuable and interesting information on microchemical identification techniques is provided.

The bulk of the book is taken up by a series of tables, the largest of which is concerned with identification data for nearly a thousand medicinal chemicals by means of the Kofler hot stage. A second table of melting points and eutectics is provided for use with the Kofler hot bench. A third table provides an alphabetical list of melting points for both the microscopically observed hot stage and the hot bench.

It is manifestly impossible for the pharmacist, who is responsible for the reliable identification of those of his drugs which are not in a form ready for use, to purchase all the expensive equipment prescribed by pharmacopoeial authorities, and the thermomicroscopic techniques are offered as the best available substitute. If the pharmacist conscientiously carries out the procedures (and heeds the warnings) detailed in this book, the identity of a very large number of labelled drugs could be confirmed satisfactorily in the pharmacy itself. The book is well produced and illustrated, and can be recommended as an aid not only to practising pharmacists, but to forensic science laboratories and to the research analysts of pharmaceutical manufacturing houses.

W. H. Stephenson (Nottingham)

M. Orchin and H. H. Jaffe, *Symmetry, Orbitals and Spectra*, Wiley–Interscience, New York, 1971, xiii+396 pp., suppl. 220 pp., price £7.70 and £2.80 (supplement).

Those prolific and energetic authors, Professors Orchin and Jaffe have combined the experiences gained in producing earlier texts on molecular symmetry, bonding and electronic spectroscopy to produce a new "three-in-one" text suitable for graduate students of all ages. A rather large proportion of the text bears a very close similarity to the previous books but the new one is supplemented by chapters introducing vibrational spectroscopy, orbital and state correlation diagrams, approximate self-consistent molecular orbital methods and a set of problems, the answers to which form a separate supplementary volume. There is an extended discussion of symmetry orbitals and electronic transitions in inorganic complexes and a very cursory dalliance with organic photochemistry. For a book that is dedicated to graduate students, its rate of climb in the first three chapters is painfully slow, though in a teaching text perhaps this can be excused. The discussion of photochemical mechanisms on the basis of symmetry correlation rules may be treacherous in view of the possibility of radiationless transitions from excited states and the all-valency-electron molecular orbital calculations which are currently so popular receive very little attention. Undoubtedly the most useful features of the book are the supplementary volume of worked problems and the long discussion relating to inorganic complexes. Unfortunately, from the point of view of the beginner the book goes too far, and from the point of view of the enthusiast or the advanced student it starts too slowly, and travels a long way in some directions but nothing like far enough in others.

J. P. Simons (Birmingham)

Preparative Gas Chromatography, Edited by A. Zlatkis and V. Pretorius, Wiley–Interscience, New York, 1971, viii + 402 pp., price £8.50.

Many chemists are asking whether the scaling up of g.l.c. to an industrial dimension is generally economically viable and when we can expect it to happen. Perhaps the evident success of g.l.c. as a separation tool on a micro and submicro scale in modern analytical chemistry has blinded us to the potential of the technique as a method for isolating or recovering pure chemical compounds on a large scale.

There are many problems associated with increasing the size of the operation; many of the current theories of g.l.c. depend on an adherence of the systems to conditions which approach ideality. It is assumed that equilibration of the solutes between the mobile and stationary phases occurs immediately, also that the capacity of any particular part of the stationary phase is not exceeded for any one solute. The relative efficiencies of systems are deduced from such principles. On a large scale it is extremely unlikely that such conditions will obtain and new basic theories will be needed to give guidance to the designers and manufacturers.

The various types of column materials, both for the fabrication and the filling of the columns, assume somewhat different relative values when considered at this scale. Packing materials require different physical properties before they can be considered suitable.

Scaling up must include the study of whether the technique can better be exploited as a batch process, or as a continuous process, with the attendant maintenance problems. Automatic control of both solute and mobile phase flows becomes imperative. Instrumentation may have to be further developed to ensure optimum efficiency of the process.

All these points and others are dealt with in a very authoritative but reasoned manner by the various contributors. Three of the ten chapters deal with the applications in organic chemistry, flavour research and biomedical and biochemical applications. This scale-up is from microgramme to gramme size. It would have been useful to have examples of much larger, say kilogramme, samples. Even speculation about these sizes would have been interesting.

The book is well arranged with a useful index. I can recommend it for all who deal with g.l.c. and with the isolation of pure substances. For some it may confirm their views, for others it may be the beginning of new ideas and new research programmes.

L. S. Bark (Salford)

Comprehensive Analytical Chemistry, Edited by C. L. Wilson and D. W. Wilson, *Vol. II C, Electrical Methods; Physical Separation Methods*, Elsevier, Amsterdam, 1971, xvi+420 pp., price Dfl. 95.00 (*ca.* $28.00).

The latest book in this series has four sections. They deal with thin layer and paper chromatography (129 pp.), radiochemistry (76 pp.), n.m.r. and e.s.r. (112 pp.) and X-ray spectrometry (82 pp.). In the tradition of this series, all the articles are well-written and provide clear introductions to their respective subjects. The chromatography chapter is comprehensive, although separations of inorganic materials are considered only briefly. It is probably, also, the most up-to-date of the articles, and contains a very few references as late as 1969. This contrasts with the radiochemistry chapter, which deals with the literature only up to 1966. Nevertheless, this particular review is a remarkably concise account of a very wide field (tracer methods, activation analysis, radiometric methods, isotope dilution analysis, safety aspects). The n.m.r./e.s.r. chapter provides a good background account of the techniques, and is especially welcome for the genuine analytical applications that are described, and the bibliography of books and review articles. The X-ray spectrometry chapter disappointingly does not deal with diffraction, but is otherwise comprehensive. Like the n.m.r. chapter, references to 1968 literature are included, but aspects that have recently achieved prominence such as computer control and correction are only touched upon.

The delay in publishing some of the material in this book has undoubtedly arisen from the original intention that each volume should deal with related topics. The present voume, however, has already deviated from this path in including chromatography and "electrical" methods within one cover (and, indeed, calling radiochemical methods, for example, an electrical method). Why not let the series become completely flexible—in the interest of up-to-date publication—and become completely non-systematic in the topics included?

A. Townshend (Birmingham)

K. H. Obst, W. Münchberg und H. Malissa, *Elektronenstrahl-Mikroanalyse (ESMA) zur Untersuchung basischer feuerfester Stoffe*, Monographs in Applied Mineralogy, Vol. 2, Springer-Verlag, Wien–New York, 1972, xi + 125 S., Preis DM 65,—.

Nachdem in den letzten Jahren eine Reihe von Werken über die Elektronenstrahl-Mikroanalyse (ESMA) im allgemeinen erschienen ist, beschreibt die vorliegende Monographie nun die Anwendung der ESMA auf dem Gebiet der basischen feuerfesten Stoffe, welche bei der modernen Stahlherstellung und in der Steine- und Erdenindustrie grosse Bedeutung besitzen.

Der erste Abschnitt (22 S.) gibt einen kurzgefassten Überblick über die angewandten Methoden zur Untersuchung feuerfester Materialien: Lichtmikroskopie, Transmissions-, Absorptions-, Reflexions- und Emissionselektronenmikroskopie, Röntgenemissionsspektralanalyse, Röntgendiffraktion, Mikroradiographie und Kathodenlumineszenz. Der zweite Abschnitt (32 S.) befasst sich mit den allgemeinen Grundlagen der ESMA. Nach Darstellung der nötigen theoretischen Grundlagen wird der prinzipielle Aufbau der Geräte kurz beschrieben und anschliessend auf die Präparation der zu untersuchenden Proben und die Messtechnik eingegangen. Den Abschluss bilden Kapitel über die Anwendung und Herstellung von Standardproben sowie die Auswertung der Messdaten und deren Korrektur.

Im dritten Abschnitt (16 S.) wird der Einsatz der ESMA auf dem Gebiet der Phasenanalyse von Zwei- und Dreistoffsystemen ($CaO–SiO_2$, $CaO–MgO–SiO_2$, $CaO–FeO_n$ und CaO–SrO) und ihre Bedeutung für die schnelle Ermittlung von eutektischen Punkten, Rinnen, Konoden und Konodendreiecken erläutert. Der letzte Abschnitt (39 S.) bringt Beispiele zur Anwendung der ESMA bei der Untersuchung feuerfester technischer Produkte, die vor allem für den Praktiker von besonderem Interesse sind. Nach einer Übersicht über die Einteilung der feuerfesten Stoffe wird im einzelnen auf Produkte aus Sinterdolomit, Sintermagnesit, Chromit und Chrommagnesit sowie auf Kohlenstoffsteine, Zirkonsteine und Siliciumcarbid eingegangen. Es werden vor allem Ergebnisse von ESMA-Untersuchungen mittels Flächen-, Linien- und Punktanalyse gebracht und mit Hilfe zahlreicher Lichtmikroskop- und ESMA-scanning-Bilder und Tabellen der Aufbau der Stoffe vor und nach ihrem Einsatz beschrieben und diskutiert. Die angeführten Ergebnisse stammen durchweg aus neuerer Literatur und zum Teil von den Autoren der Monographie. Die Literatur zitiert rund 170 Veröffentlichungen, die jeweils am Ende der einzelnen Kapitel angeführt sind und zu *ca.* 85% aus dem Zeitabschnitt 1960–1970 und zu *ca.* 15% aus den Jahren 1950–1960 stammen.

Nach dem der Monographie beigefügten Begleittext soll diese einerseits den Operator der ESMA über die Probleme der Feuerfeststoffe und andererseits den Feuerfest-Fachmann über die durch die ESMA sich bietenden Möglichkeiten orientieren. Dieser Aufgabe wird das Buch gerecht. In seiner Ausführung zeigt das Buch den vom Springer-Verlag her bekannten Standard, während der etwas hoch erscheinende Preis wohl auf die grosse Zahl der Abbildungen zurückzuführen sein dürfte. Im Hinblick auf die Zielsetzung der Monographie und den gebotenen Stoff kann das Buch dem an der Untersuchung und Anwendung der basischen Feuerfeststoffe interessierten Anwenderkreis allgemein empfohlen werden.

O. G. Koch (Neunkirchen/Saar)

R. Pribil, *Analytical Applications of EDTA and Related Compounds*, Pergamon Press, Oxford, 1972, xvii + 368 pp., price £ 12.50.

From a glance at this title, the casual reader may conclude that here is yet another treatise on the conventional uses of polyaminopolycarboxylic acids as titrimetric reagents. Such a conclusion would be totally wrong, and this publication has little in common with the author's original Czech editions of 1953 and 1957. It is, in fact, an up-to-date publication from an entirely new manuscript in which the emphasis is on the use of these compounds as ancillary screening (masking) reagents, to improve the selectivity of established reactions in quantitative analytical chemistry.

In the first chapter, R. Belcher and A. Townshend succinctly summarise the evolution and early development of ethylenediaminetetraacetic acid (EDTA) as an analytical reagent. In Chapter 2, the characteirstic reactions of EDTA and its related complex-forming compounds, are discussed, and this provides an excellent precursor to a better understanding of the fundamental equilibria referred to, or implied in, the subsequent text. The remaining four chapters (Part II) deal exclusively with analytical applications.

Chapter 3, on *Gravimetric Analysis*, is divided equally between precipitation reactions with inorganic and organic reagents. The three main sections of Chapter 4, *Titrimetric Analysis*, cover alkalimetry, redox methods, and precipitation titrations. Some metallochromic indicators resemble EDTA structurally, the most important being those derived from the triphenylmethane dyes, *e.g.*, methylthymol blue and thymolphthalexone; in Chapter 5, on *Colorimetry*, their uses as colorimetric reagents are described extensively. The final Chapter has the title *EDTA as a Masking Agent in Colorimetry*.

This brief summary hardly does justice to the wealth of first-hand information and expert comment contained in the book, but it should whet the appetite of those for whom this fascinating group of compounds has such a variety of known and potential applications. The author is to be congratulated on the appearance of his latest release, which is presented in a commendably clear style, with hundreds of supporting references; additional qualities that should sway any hesitant purchaser of the book.

It is unfortunate that authoritative monographs like this one, are, perhaps understandably, expensive, and hence are not always within easy reach of the younger generation who would especially benefit from this comprehensive coverage of the subject.

W. T. Elwell (Birmingham)

PUBLICATIONS RECEIVED

NATIONAL BUREAU OF STANDARDS PUBLICATIONS

Solid-State Chemistry, Edited by R. S. Roth and S. J. Schneider, Jr., Proc. of a Symposium held at N.B.S., Gaithersburg, October, 1971, N.B.S. Spec. Publ. 364, July 1972, 799 pp., price $ 7.50.

Science of Ceramic Machining and Surface Finishing, Edited by S. J. Schneider, Jr. and R. W. Rice, Proc. of a Symposium sponsored by the American Ceramic Society, O.N.R. and N.B.S., Gaithersburg, November, 1970, N.B.S. Spec. Publ. 348, May 1972, 431 pp., price $5.25.

Organic Chemistry Section: Summary of Activities, June 1970–June 1971, Edited by R. Schaffer, N.B.S. Tech. Note 587, August 1972, 131 pp., price $1.25.

C. N. R. Rao and M. Natarajan, *Crystal Structure Transformations in Binary Halides*, N.B.S. Publ. NSRDS-NBS 41, 1972, 53 pp., price 55 cents.

H. G. McAdie, P. D. Garn and O. Menis, *Standard Reference Materials: Selection of Differential Thermal Analysis Temperature Standards*, N.B.S. Spec. Publ. 260-40, August 1972, 71 pp., price 65 cents.

Takehiko Shimanouchi, *Tables of Molecular Vibrational Frequencies: Consolidated Volume*, N.B.S. Publ. NSRDS-NBS 39, June 1972, 164 pp., price $3.00.

L. L. Sparks, R. L. Powell and W. J. Hall, *Reference Tables for Low-Temperature Thermocouples*, N.B.S. Monograph 124, June 1972, 61 pp., price 60 cents.

K. F. J. Heinrich, R. L. Myklebust, H. Yakowitz and S. D. Rasberry, *A Simple Correction Procedure for Quantitative Electron-Probe Microanalysis*, N.B.S. Tech. Note 719, May 1972, 49 pp., price 55 cents.

J. I. Schultz, R. K. Bell, T. C. Rains and O. Menis, *Standard Reference Materials: Methods of Analysis of N.B.S. Clay Standards*, N.B.S. Spec. Publ. 260-37, June 1972, 86 pp., price 75 cents.

L. Hagan and W. C. Martin, *Bibliography on Atomic Energy Levels and Spectra, July 1968–June 1971*, N.B.S. Spec. Publ. 363, June 1972, 103 pp., price $1.00.

Metric Conversion Card, N.B.S. Spec. Publ. 365, July 1972, price 10 cents each or $6.25 per 100.

Activation Analysis: A Bibliography through 1971, Edited by G. J. Lutz, R. J. Boreni, R. S. Maddock and J. Wing, N.B.S. Tech. Note 467, August 1972, 467 pp., price $7.00.

The above publications can be ordered prepaid from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Foreign remittances must be in U.S. exchange and should include 25% of the price to cover postages.

ANALYTICA CHIMICA ACTA, VOL. 64 (1973)

AUTHOR INDEX

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(Continued from page 4 of cover)

VOL. 64 NO. 3 ANALYTICA CHIMICA ACTA May 1973

CONTENTS

(continued on inside page of cover)