

CHROM. 9089

CHLORINATION AND GAS CHROMATOGRAPHIC DETERMINATION OF ARSENIC IN OXIDES, SULPHIDES, ORES AND ALLOYS

B. IATRIDIS and G. PARISSAKIS

Inorganic and Analytical Chemistry Department, National Technical University of Athens, Athens 147 (Greece)

SUMMARY

A simple, sensitive, selective, accurate and rapid method for the quantitative determination of arsenic in oxides, sulphides, ores and alloys is described. The method is based on the chlorination of arsenic-containing compounds with carbon tetrachloride in a sealed glass tube. Under specific conditions, the chlorination is quantitative and rapid. The volatile products are introduced into the gas chromatographic system after crushing the tube in a special device.

The method gives results in a very short time (*ca.* 10 min), involves simple manipulations, is especially suitable for automation and the error is of the order of $\pm 0.5\%$.

INTRODUCTION

The quantitative determination of arsenic in different materials by classical methods of analysis is a laborious, time-consuming and concentration-dependent procedure. Using instrumental methods to carry out this determination, several problems arise, *e.g.*, fusion of the sample and interference from other elements.

The advantages of gas-liquid chromatography (GLC) (versatility, reliability, speed, small sample requirement, simplicity in operation and low equipment cost) can help the analysis of transition-element compounds if they can be easily converted quantitatively into volatile compounds. In previous work^{1,2}, it was shown that a number of elements, when converted into their volatile metal chlorides, can be readily separated and determined via GLC by an appropriate choice of packing material, chromatographic parameters and the application of special techniques. In this paper, a simple, sensitive, selective and rapid method for the determination of arsenic in a wide variety of its compounds (oxides, sulphides, ores, alloys) over a wide concentration range (0.77-76%) is presented. The arsenic is converted into the corresponding chloride with carbon tetrachloride and then determined by GLC.

The choice of carbon tetrachloride as chlorinating agent was dictated mainly by its double action on compounds that contain oxygen or sulphur and its inertness towards the column packing materials, even if it is used in excess. Moreover, the by-products formed (COCl_2 , Cl_2) during the chlorination process act as chlorinating

agents themselves. The thermal decomposition products of carbon tetrachloride (except hexachloroethane^{3,4}) appear in very small amounts. All of these by-products give peaks that have retention times different from those of the chlorides under consideration.

The development of this procedure necessitated a thorough study of the chlorination reaction of arsenic compounds. Optimal chlorinating conditions were ascertained and the by-products were identified. The chlorination of arsenic compounds with carbon tetrachloride was reported by Camboulives⁵ for arsenic trioxide in an open system.

EXPERIMENTAL

Reagents and materials

Arsenic trichloride used for the preparation of the calibration graphs was obtained from commercial sources. It was purified by isothermal distillation and was kept under anhydrous conditions. Arsenic trioxide and arsenic trisulphide (analytical-reagent grade) were obtained from Alpha Ventron (Beverly, Mass., U.S.A.).

Chemical analysis of and X-ray diffraction measurements on erythrite, antimony concentrate, copper ore and lead ore, gave the following results.

(a) *Erythrite*. As, $30.78 \pm 0.01\%$; Co, $18.85 \pm 0.03\%$; Ni, $14.76 \pm 0.03\%$; Fe, $6.51 \pm 0.05\%$; Cu, $0.76 \pm 0.04\%$; Al, $0.90 \pm 0.05\%$; and SiO_2 , $3.15 \pm 0.05\%$. Components: $\text{Ni}_3\text{As}_2\text{O}_8$, Ni_2As , NiAs_2 , FeAs , $\text{Co}_3\text{As}_2\text{O}_8$, Co_2As , CoAs_2 , CoNi and SiO_2 .

(b) *Antimony concentrate*. Sb, $60.50 \pm 0.03\%$; As, $0.89 \pm 0.01\%$; Fe, $1.16 \pm 0.06\%$; Cu, $0.21 \pm 0.04\%$; Pb, $0.03 \pm 0.01\%$; Al, $1.06 \pm 0.04\%$; and SiO_2 , $9.80 \pm 0.05\%$. Components: Sb_2S_3 , As_2S_3 , Sb_2O_3 , As_2O_3 , AsSbS_3 , $\text{Cu}_3(\text{SbAs})\text{S}_4$, PbSb_2S_4 , FeAsS , CuSbS_2 , etc.

(c) *Copper ore*. As, $0.91 \pm 0.01\%$; Cu, $9.65 \pm 0.04\%$; Pb, $0.11 \pm 0.01\%$; SiO_2 , $7.95 \pm 0.05\%$; S, $35.57 \pm 0.01\%$; BaSO_4 , $5.63 \pm 0.04\%$; Fe, $27.65 \pm 0.05\%$; and Al_2O_3 , $1.31 \pm 0.05\%$. Components: CuFeS_2 , FeAsS , Cu_2As_3 , $\text{Cu}_2\text{As}_2\text{O}_7$, CuSO_4 , etc.

(d) *Lead ore*. As, $9.10 \pm 0.01\%$; Pb, $18.30 \pm 0.01\%$; S, $21.80 \pm 0.01\%$; Fe, $19.80 \pm 0.05\%$; Zn, $3.20 \pm 0.04\%$; and SiO_2 , $13.30 \pm 0.05\%$. Components: As_2O_3 , As_2S_3 , FeAsS , FeAsO_4 , $\text{Zn}_3(\text{AsO}_3)_2$, PbO , $\text{PbO} \cdot \text{PbSO}_4$, ZnSO_4 , FeS_2 , $2\text{PbO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{SiO}_2$, etc.

The components of the alloys tested had the following concentrations.

(i) *Babbit alloy*. As, $1.00 \pm 0.01\%$; Sb, $15.00 \pm 0.03\%$; Sn, $1.00 \pm 0.05\%$; Cu, $0.50 \pm 0.04\%$; and Pb, balance.

(ii) *Shot alloy*. As, $0.77 \pm 0.01\%$; Sb, $3.45 \pm 0.03\%$; and Pb, balance.

Sample preparation, chlorination technique and gas chromatographic determination

A borosilicate tube (4 cm long, 6 mm O.D., 4 mm I.D.), sealed at one end, cleaned and dried at 130° , was used as a reaction tube. To carry out a preparation, the tube was weighed and dried at 140° , and powdered sample (400–600 mesh) is introduced. As soon as the necessary amount (Tables I–III) of sample had been inserted, the open end of the tube was closed with adhesive tape and dry nitrogen was blown around this area.

TABLE I
QUANTITATIVE DETERMINATION OF ARSENIC TRIOXIDE

Sample No.	As ₂ O ₃ taken (mg)	As ₂ O ₃ found (mg)	Difference (mg)	Error (%)
1	3.19	3.18	-0.01	-0.31
2	2.68	2.64	-0.04	-1.49
3	5.35	5.38	+0.03	+0.56
4	3.28	3.29	+0.01	+0.30
5	2.72	2.70	-0.02	-0.73
6	4.60	4.61	+0.01	+0.22
				Average: -0.24
				Standard deviation: ±0.8

TABLE II
QUANTITATIVE DETERMINATION OF ARSENIC TRISULPHIDE

Sample No.	As ₂ S ₃ taken (mg)	As ₂ S ₃ found (mg)	Difference (mg)	Error (%)
1	11.55	11.48	-0.07	-0.61
2	9.07	8.99	-0.08	-0.88
3	9.15	9.24	+0.09	+0.98
4	10.13	10.08	-0.05	-0.50
5	8.69	8.60	-0.09	-1.00
6	10.49	10.56	+0.07	+0.66
7	6.98	6.93	-0.05	-0.71
				Average: -0.29
				Standard deviation: ±0.78

TABLE III
DETERMINATION OF ARSENIC IN ORES AND ALLOYS

Sample	Weight (mg)	No. of determinations	As (% w/w)		Error
			Present	Found ± standard deviation	
Erythrite	3.5-6.0	8	30.78	30.34 ± 0.27	-0.44
Antimony concentrate	14.0-29.0	6	0.89	0.88 ± 0.03	-0.01
Copper ore	41.0-56.5	6	0.91	0.89 ± 0.01	-0.02
Lead ore	33.0-40.0	6	9.10	9.00 ± 0.10	-0.10
Babbitt alloy	15.5-19.5	8	1.00	0.98 ± 0.01	-0.02
Shot alloy	26.0-35.0	6	0.77	0.74 ± 0.02	-0.03

The lower part of the tube, which was held in a vertical position, was placed in a container of dry-ice and the corresponding amount of dry carbon tetrachloride (Table IV) was added. The tape was then removed, the open end sealed and the tube withdrawn from the cold bath. Each reaction tube was then placed in an oven at 575° for a given time (Table IV). In order to introduce the sample into the GLC system, a special crushing device¹ was constructed. The borosilicate capsule containing the chlorinated sample was placed inside this apparatus, which was connected to the

TABLE IV

CHLORINATION OF AND GAS CHROMATOGRAPHIC CONDITIONS FOR VARIOUS ARSENIC SAMPLES

Sample	CCl_4 added (μ l per mg of sample)	Chlorination time at 575° (min)	Chromatographic conditions				Flow-rate carrier gas (ml/min)
			Temperature ($^\circ$ C)				
			Crushing device	Injection port	Column	Detector	
As_2O_3	1.5	5	150	150	150	100	24
As_2S_3	1.1	6	150	150	150	100	19
Erythrite	1.5	20	250	230	150	200	30
Antimony concentrate	1.0	15	250	230	150	200	30
Copper ore	0.5	15	250	230	150	100	24
Lead ore	0.6	15	250	230	150	100	24
Rabbit alloy	0.5	6	250	230	150	100	30
Shot alloy	0.5	6	250	230	150	100	30

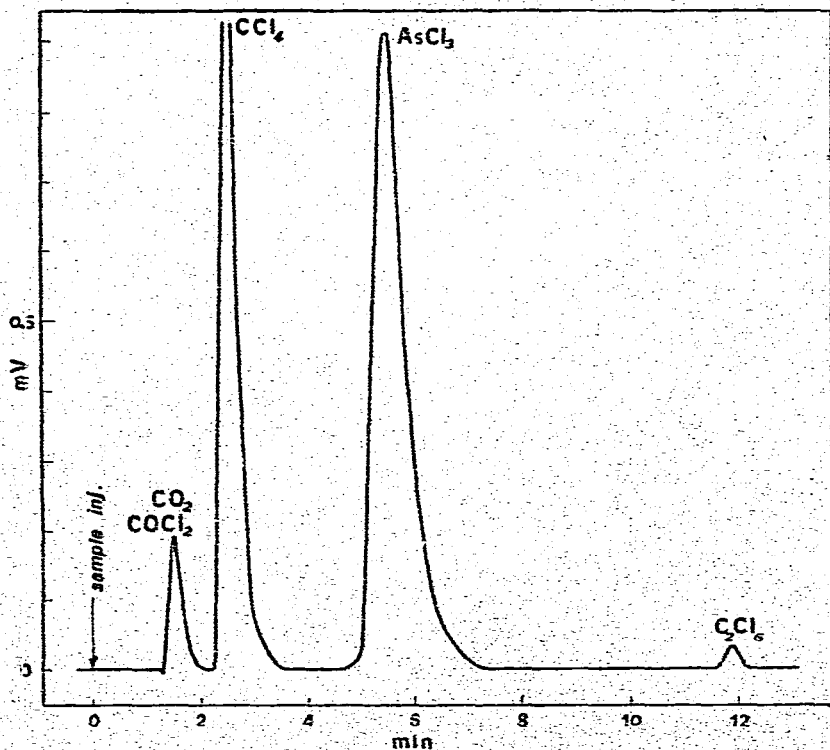


Fig. 1. Chromatogram of chlorination of As_2O_3 with CCl_4 (6 min, 575°). Glass column (183 cm long, O.D. 6 mm, I.D. 4 mm). Packing material: silicone oil DC-550, 10% (w/w) on Celite 545. Carrier gas (N_2) flow-rate: 24 ml/min. Detector: TCD (Gow-Mac 4, tungsten filaments); bridge current, 150 mA. Temperatures: capsule chamber, 150° ; injection port, 150° ; column, 150° ; detector, 100° .

injection port of the chromatographic unit. After being heated, the sample tube was broken by the plunger. The exposed sample in the hot crushing device was then swept into the column by the carrier gas.

The crushing device used, which is a variation of similar existing devices⁶, accepts sample holders of various types and sizes. It can be used for gases, liquids, solids and, in general, for samples that consist of heterogeneous systems. It is also possible for the device itself to serve as a micro-reactor.

Silicone oil DC-550, 10 and 20% (w/w) on Celite 545, was used as the column packing material, which permits very good resolution for a number of pairs of chlorides⁷.

A Hewlett-Packard 700 gas chromatograph equipped with a thermal conductivity detector (TCD) (Gow-Mac 4, tungsten filaments) was used, modified by us in order to keep the oven temperature constant to within $\pm 0.1^\circ$. Nitrogen was used as the carrier gas and was dried by passing it through an activated molecular sieve and P_2O_5 traps at flow rates of 10–100 ml/min. This detector showed a response variation toward inorganic chlorides. From time to time, the detector was washed with acetone and hydrochloric acid solution in order to prevent alteration of the response due to deposits of hydrolysis or reaction products.

Glass columns (183 cm long, 6 mm O.D., 4 mm I.D.) were used in order to prevent reaction with the highly corrosive chlorides. All columns were packed under anhydrous vacuum conditions by inserting Pyrex glass-wool at one end of the column, applying a vacuum to that end and adding the packing material at the other end. The column was vibrated and the vacuum continued until the packing material

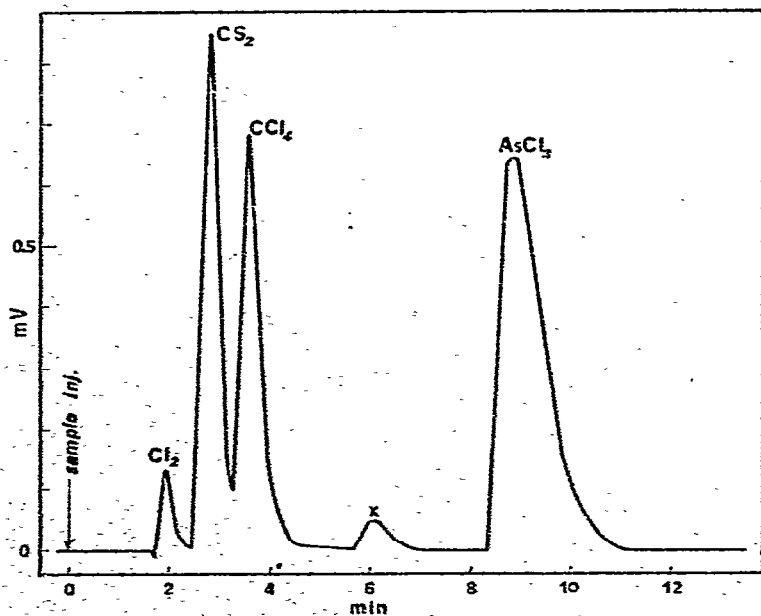


Fig. 2. Chromatogram of chlorination of As_2S_3 with CCl_4 (6 min, 575°). Packing material: silicone oil DC-550, 20% (w/w) on Celite 545. Carrier gas (N_2) flow-rate: 19 ml/min. Other conditions as in Fig. 1.

did not settle any further. The columns were conditioned overnight at the maximum recommended temperature of 150° . The effluent end of the column was not connected to the detector during the conditioning period. The column oven temperatures used were at most 30° below the maximum recommended temperature limit for isothermal conditions. The chlorinating and chromatographic conditions are given in Table IV.

RESULTS AND DISCUSSION

During the chlorination of arsenic compounds with carbon tetrachloride, not only the conversion of arsenic into arsenic trichloride occurs, but also a number of by-products are formed. These by-products are derived mainly from oxygen- and sulphur-containing compounds (COCl_2 , CO_2 , CS_2 , Cl_2) and to a much lesser extent from the thermal decomposition of the chlorinating agent (C_2Cl_6 , C_6Cl_6 , etc.). The optimal chlorination conditions were determined by a study of the conversion efficiency as a function of chlorination times and temperatures, similar to that carried out for arsenic trioxide².

Fig. 1 shows a typical chromatogram of the reaction products of carbon tetrachloride with arsenic trioxide. The first peak arises from two components: carbon dioxide and phosgene. The second peak is attributed to an excess of carbon tetra-

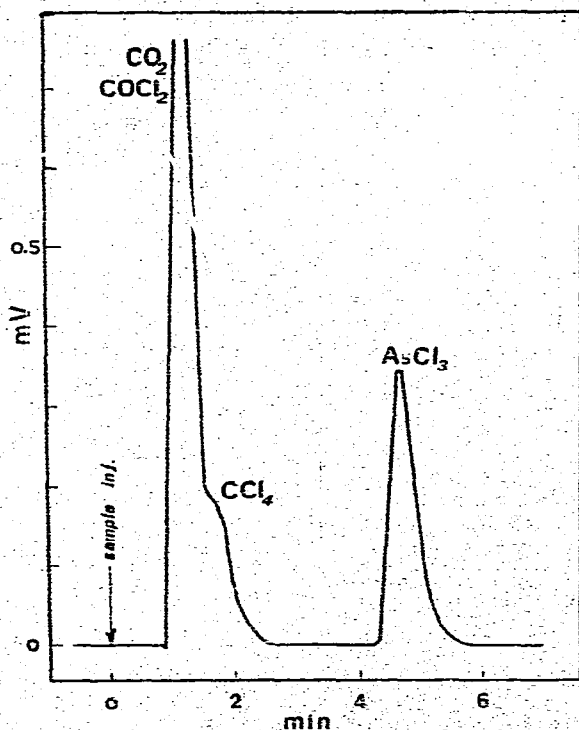


Fig. 3. Chromatogram of chlorination of erythrite with CCl_4 (6 min, 575°). Carrier gas (N_2) flow-rate: 30 ml/min. Temperatures: capsule chamber, 250° ; injection port, 230° ; column, 150° ; detector, 300° . Other conditions as in Fig. 2.

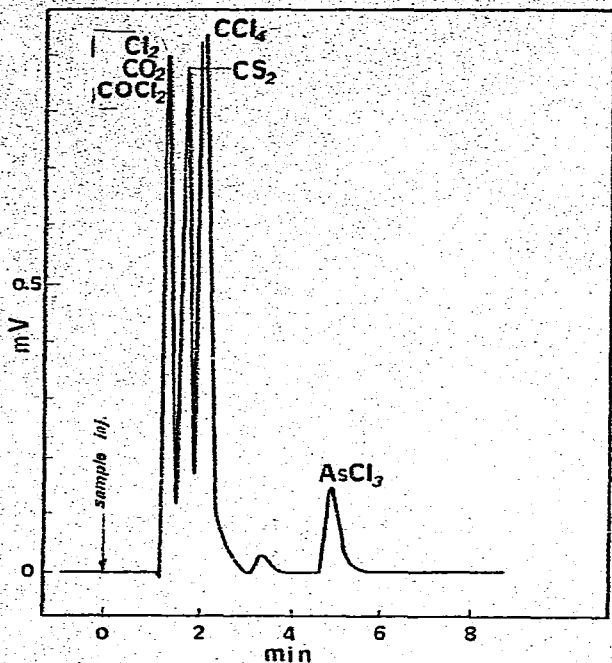


Fig. 4. Chromatogram of chlorination of antimony concentrate with CCl_4 (6 min, 575°). Conditions as in Fig. 3.

chloride, the third is due to arsenic trichloride and the last to hexachloroethane. Under the chromatographic conditions used, no peaks were observed at times longer than 15 min.

Fig. 2 is a typical chromatogram of the reaction of carbon tetrachloride with arsenic trisulphide. All peaks, except the unknown peak (\times), were identified by different analytical methods.

Fig. 3 represents a chromatogram of the reaction products of carbon tetrachloride with erythrite and Fig. 4 shows a chromatogram of the chlorination of antimony concentrate with carbon tetrachloride.

Fig. 5 is a chromatogram of the chlorination reaction of carbon tetrachloride with copper ore; the same type of chromatogram was obtained by the chlorination of lead ore with carbon tetrachloride.

Fig. 6 shows the peaks obtained after the chlorination of Babbit alloy with carbon tetrachloride. All the components were identified, except that which gave peak \times .

Chlorine and carbon tetrachloride in all of the above chromatograms were identified by their infrared spectra after collecting the fractions at the outlet of the column. Tin tetrachloride and arsenic trichloride peaks were confirmed by comparison of their retention times with those of authentic samples.

The chromatogram of the chlorination reaction of carbon tetrachloride with Shot alloy in a sealed glass tube is identical with that of Babbit alloy without the tin tetrachloride peak. By using silicone oil, the resulting peaks showed a slight tailing

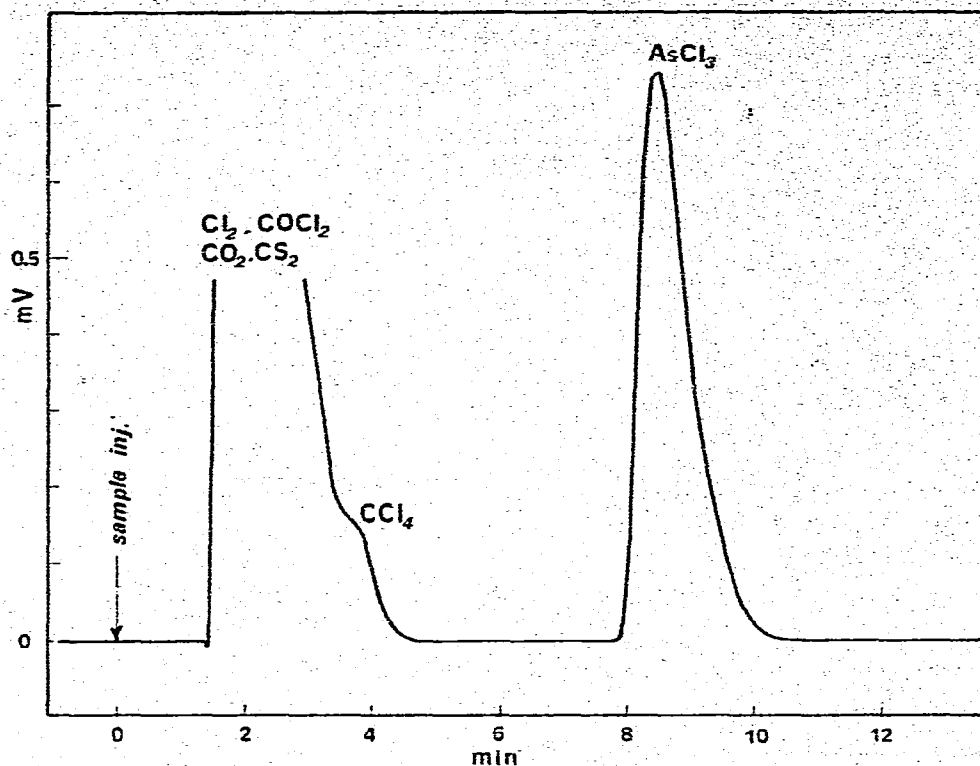


Fig. 5. Chromatogram of chlorination of copper (or lead) ore with CCl_4 (6 min, 575°). Carrier gas (N_2) flow-rate: 24 ml/min. Detector temperature: 100° . Other conditions as in Fig. 3.

which is attributed⁸ not to the chemical composition of this liquid phase but to the inadequate silanization of the solid support. The chlorine produced during the chlorination reaction had no effect on the liquid phase⁹ as its amount was limited¹⁰.

The area under the arsenic trichloride peak was measured by trapezoid construction¹¹.

The maximum detector sensitivity was 1000 mV ml/mg during all determinations. The calibration graphs were linear for arsenic within the range of 0.1–8 mg. The baseline drift during a single run and also during 24 h of continuous operation was negligible (less than 0.01 mV for 1 mV full-scale deflection of the recorder).

It is clear that the characteristics of the method described, the simplicity of the whole process, especially the simple procedure for sample preparation, and also the short time required for measurement, its accuracy and the low cost of the instrumentation used, make it superior to existing methods. Thus, it competes favourably with the iodimetric method in the accuracy and the sample sizes used¹², with emission spectroscopy in view of the accuracy over an extended range of arsenic concentrations (0.77–76%)¹³ and with other methods that require either expensive instrumentation or special accessories to existing apparatus, such as the use of atomic-absorption spectrophotometry for the determination of arsenic.

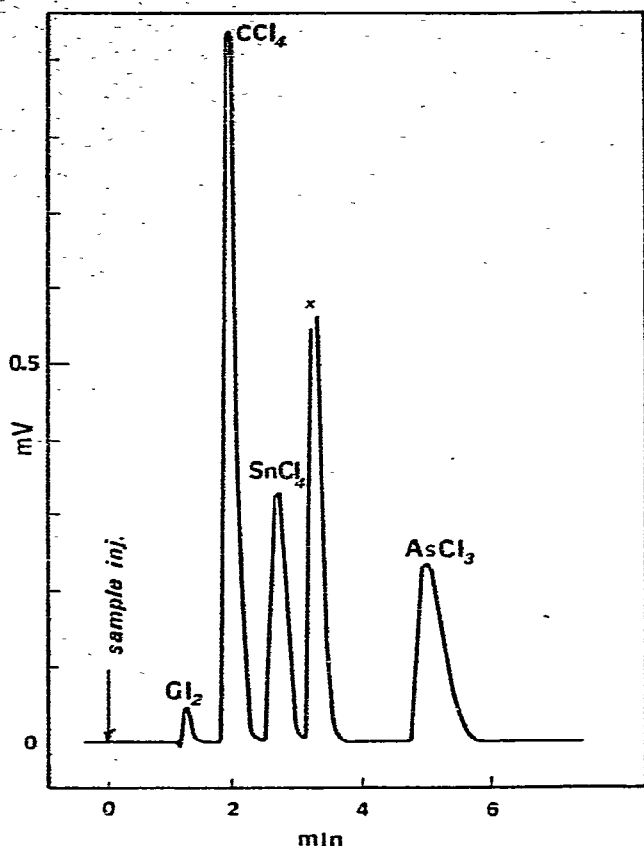


Fig. 6. Chromatogram of chlorination of Babbit alloy with CCl_4 (6 min, 575°). Conditions as in Fig. 3.

ACKNOWLEDGEMENT

The authors thank the General Cement Company, AGET, Athens, Greece, for a research grant which made this work possible.

REFERENCES

- 1 G. Parissakis and B. Iatridis, *J. Chromatogr. Sci.*, 12 (1974) 737.
- 2 B. Iatridis, *Doctoral Dissertation*, National Technical University, Athens, 1974.
- 3 M. C. le Moan, *C.R. Acad. Sci., Paris*, (1962) 2462.
- 4 S. Tsuge, J. J. Leary and T. L. Isenhour, *J. Chem. Educ.*, 51 (1974) 266.
- 5 P. Camboulives, *C.R. Acad. Sci., Paris*, 150 (1910) 175.
- 6 O. Mlejnek and J. Blatnický, *J. Chromatogr.*, 105 (1975) 382.
- 7 G. Parissakis, D. Vrantí-Piscou and J. Kontoyannakos, *Chromatographia*, 3 (1970) 541.
- 8 G. Parissakis, D. Vrantí-Piscou and J. Kontoyannakos, *J. Chromatogr.*, 52 (1970) 461.
- 9 S. T. Sie, J. P. A. Bleumer and G. W. A. Rijnders, *Separ. Sci.*, 1 (1966) 41.
- 10 G. Parissakis, D. Vrantí-Piscou and J. Kontoyannakos, *Z. Anal. Chem.*, 254 (1971) 188.
- 11 L. Condal-Bosch, *J. Chem. Educ.*, 41 (1964) A235.
- 12 G. Charlot, *Les Méthodes de la Chimie Analytique, Analyse Quantitative Minérale*, Masson, Paris, 1968, p. 605.
- 13 A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1966, p. 856.