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GAS CHROMATOGRAPHIC DETERMINATION OF TIN IN OXIDES, SULPHIDES, MINERALS AND ALLOYS AFTER CHLORINATION

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SUMMARY

A method is described for the determination of tin in alloys, in its sulphides, oxides and other compounds which requires a time of less than 12 min per sample. The method is not only fast but accurate and precise, possessing a relative accuracy and precision better than −0.36% and 0.71%, respectively. It is also selective and specific since other elements giving volatile and thermally stable chloro compounds do not interfere, and a 10^{-5} g amount of Sn can be detected. Moreover, it can be applied to tin levels from 1 to 99%. The tin-bearing material and carbon tetrachloride are introduced into a glass capsule where the chlorination reaction takes place at high temperature.

INTRODUCTION

A feasibility study has been made[1,2] of the use of gas chromatography (GC) for the separation and determination of volatile chlorides of certain chemical elements. It has been shown that by using gas–liquid chromatography (GLC) under certain conditions it is possible to separate and determine quantitatively a number of compounds such as $SnCl_4$, $GeCl_4$, $SiCl_4$, $SbCl_5$, $POCl_3$, $AsCl_3$ and $TiCl_4$. This enables the development of an analytical method for the determination of Sb, Ge[3,4] and other elements, in their oxides, sulphides and alloys. This method possesses certain advantages over other existing methods. It is sensitive, specific, selective, precise and fast. Moreover, the necessary instrumentation is almost conventional, and the manipulations involved are very simple.

A number of GC determinations of Sn has been reported by Dennison and Freund[5], Sie *et al.*[6] and Becker *et al.*[7]. In the forementioned papers, chlorine is proposed as the chlorinating agent, but by this means Sn is quantitatively converted into the volatile chlorides only in a limited number of alloys. Moreover, it has been shown that the chlorine present in the chloride phase reacts with the packing materials of the column.

In the present work carbon tetrachloride has been used as the clorinating agent and the chlorination reaction takes place in a small borosilicate glass capsule. The reducing and chlorinating ability of carbon tetrachloride extends the applicability of the proposed method to many different compounds of tin. Moreover, carbon tetrachloride is inert toward the column packing materials and when present in excess in the sample it gives a peak well resolved from any other peak of interest.

EXPERIMENTAL

Materials and reagents

Tin tetrachloride used for the construction of the calibration curves was obtained from Alfa-Ventron, (Beverly, Mass., U.S.A.). Tin oxide and tin sulphide were prepared and purified through repeated precipitations.

Tin alloys. The chemical analysis (wet chemical methods, AAS, X-ray fluorescence, etc.) of the tested alloys gave the following results (%, w/w).

(1) Phosphor bronze: Sn = 4.96 ± 0.010; Pb = 0.005 ± 0.001; Fe = 0.02 ± 0.003; P = 0.14 ± 0.002; Cu = 94.900 ± 0.040

(2) Tin–lead alloy: Sn = 1.90 ± 0.010; Pb = balance

(3) Wood's alloy: Sn = 16.00 ± 0.010; Bi = 52.50 ± 0.010; Pb = 31.50 ± 0.001

(4) Tin–lead–antimony alloy: Sn = 34.64 ± 0.010; Pb = 63.24 ± 0.002; Sb = 2.03 ± 0.010; Bi = 0.07 ± 0.010

(5) "Babbit"-alloy: Sn = 1.00 ± 0.010; As = 1.00 ± 0.010; Pb = balance; Sb = 15.00 ± 0.030; Cu = 0.50 ± 0.040

Tin Ore. The chemical analysis and X-ray measurement of tin ore indicated the presence of the compounds SnO_2, $CuFeS_2$, CuS, $CaCO_3$, SnS and FeS_2.

Sn = 5.75 ± 0.02%; Ca = 4.07 ± 0.01%; K = 1.74 ± 0.01%; Fe = 12.75 ± 0.04%; Al = 10.12 ± 0.03%; As = traces; Cu = 9.52 ± 0.04%; Ti = 2.54 ± 0.02%; C = 1.12 ± 0.01%; Si = 18.55 ± 0.05%; Zn = 2.31 ± 0.01%; S = 18.10 ± 0.01%

Sample preparation and chlorination technique

A borosilicate tube (4 cm × 6 mm O.D. × 4 mm I.D.), sealed at one end, cleaned and dried at 130°, is used as a reaction tube. A weighed amount of the sample (Tables I, II, III and V) to be analyzed is introduced as small pieces (for alloys) or in powdered form (440–600 mesh, for oxides and ores), and dried at 140°. The tube is then closed with adhesive tape and dry nitrogen is blown around this end. The lower part of the tube, which is held in a vertical position, is placed in a container of dry ice and a suitable amount of dry carbon tetrachloride (Table III) is then added. The tape is removed, the open end is sealed, and the capsule withdrawn from the cold-bath. It is then placed in an oven at 575° for the time (Table IV) required for the quantitative chlorination of the sample, before placing it in the special crushing device[8]. The capsule is broken by the plunger of the crushing device, and the liberated volatile compounds are then swept into the GC system by the carrier gas.

Calibration graphs

Calibration graphs can be obtained by two different tecniques.

(a) *Injection by syringe.* Appropriate amounts of the substance to be analyzed are injected into the GC system. Care must be taken to avoid deposition of hydrolyzed material. It is essential that the syringe is washed carefully after each use by immersing the lower part of the needle in acetone and dropping acetone simultaneously on the entrance of the plunger. The syringe is then washed with diethyl ether and dried under vacuum. Treated in this manner, one syringe can be used for a large number of injections.

(b) *By glass capsule.* Different amounts of elemental tin introduced into capsules of the same size and form used for the actual determinations are treated with the appropriate amount of CCl_4 and then submitted to GC as described above.

Apparatus

The crushing device is the sample introduction device and through it the carrier gas enters the GC system. It can accept sample holders of various types and sizes and can be used for gases, liquids, solids and in general for samples consisting of heterogeneous systems. It can also serve as a microreactor.

As column packing material, silicon oil DC 550 (20%, w/w, on Celite 545) was used because of its inertness toward $SnCl_4$ and its very good resolution for a number of chlorine compounds[2]. 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 within $\pm$ 0.1°. Nitrogen used as carrier gas was dried by passing through an activated molecular sieve and P_2O_5 traps at flow-rates of 10–100 ml/min. The detector used showed a satisfactory response toward inorganic chlorides. From time to time the detector was washed with acetone–hydrochloric acid solution in order to prevent alteration of its response owing to deposit of hydrolysis or reaction products upon the filaments. To avoid reaction with the highly corrosive chlorides, glass columns were used 183 cm × 4 mm I.D. × 6 mm O.D.).

These columns were packed under anydrous conditions by inserting glass wool at one end of the column, applying a vacuum to this end and adding the packing material from the other end. The column was vibrated and the vacuum maintained, until the packing material did not settle any further.

Columns were conditioned overnight at the maximum permitted temperature. The effluent end of the column was not connected to the detector during the conditioning period. Column oven temperatures used were at most 30° below the maximum recommended temperature limit for isothermal conditions.

RESULTS AND DISCUSSION

The conditions for the quantitative chlorination of tin in tin-bearing compounds were determined by studying the conversion efficiency as a function of time and temperature. Table I presents the results obtained for alloys which have been treated according to the proposed method. Fig 1 and 2 give the corresponding chromatograms. The GC conditions in Fig. 1 have been selected so that other volatile chloride compounds such as PCl_3 or PCl_5 in the case of phosphor bronze, or $SbCl_5$, $SbCl_3$ and Cl_2 in the case of the antimony alloy, would show a considerably different retention time compared to that of tin tetrachloride. The extent of the reaction of other constituent elements of the alloy with the clorinating agent depends on the applied conditions (time and temperature). However, under the GC conditions used these chlorides do

TABLE I

DETERMINATION OF TIN ALLOYS

Eight determinations were made in each case.

Alloy	*Weight (mg)*	*Tin (%)*			
		Present	*Found*	*S.D.*	*Error (Δ)*
Phosphor bronze	15–50	4.96	4.95	0.04	0.01
Tin–lead	18–42	1.90	1.85	0.03	0.05
Wood'sche	18–25	16.00	15.87	0.06	0.13
Tin–lead–antimony	19–42	34.64	34.30	0.14	0.34
Babbit	15–20	1.00	0.99	0.02	0.01

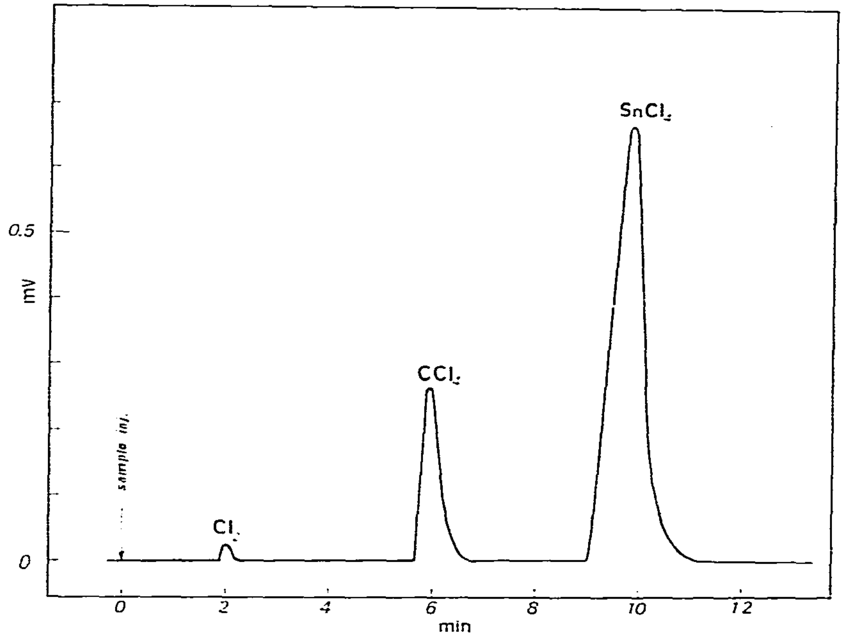

Fig. 1. Gas–liquid chromatogram for chlorination of tin alloys with carbon tetrachloride. Chromatographic conditions: glass column, 183 cm × 6 mmO.D. × 4 mm I.D.; packing material, silicon oil DC 550, 20% (w/w) on Celite 545; carrier gas (nitrogen) flow-rate, 14 ml/min; detector, TCD (Gow-Mac, 4 tungsten filaments), bridge current 150 mA. Temperatures: capsule chamber, 150°; column, 100°; detector, 100°.

not present sufficient vapour pressure to be transferred, by the carrier gas, into the column.

The method is selective, specific and free of interference from other elements. In the case of a co-determination on more than one chloride compound or when more than one chloride is produced from one element, it may be necessary to modify the chromatographic conditions. This might affect the accuracy of the proposed method.

Tables II and III present the results of the determination of tin in tin(IV) oxide and in tin sulphide and Figs. 3 and 4 give the corresponding chromatograms.

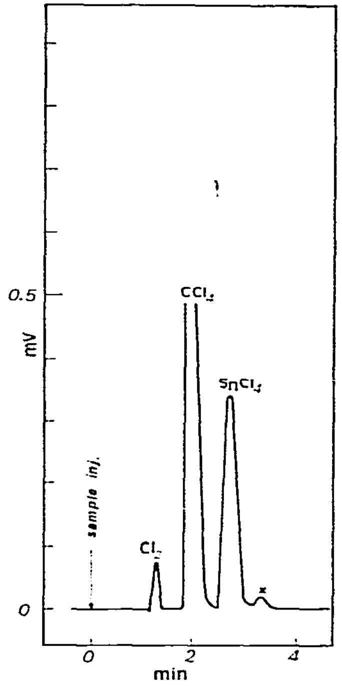

Fig. 2. Gas-liquid chromatogram for chlorination of Babbit alloy with carbon tetrachloride. Chromatographic conditions as in Fig. 1 except for carrier gas (nitrogen) flow-rate, 30 ml/min, and temperatures: capsule chamber, 250°; column, 150°; detector, 100°.

TABLE II

QUANTITATIVE DETERMINATION OF TIN IN TIN OXIDE

Weight (mg)	*Found (mg)*	*Error (mg)*	*Relative error (%)*
1.81	1.80	−0.01	−0.55
2.29	2.27	−0.02	−0.87
1.43	1.41	−0.02	−1.40
1.69	1.68	−0.01	−0.59
2.10	2.11	+0.01	+0.48
1.18	1.16	−0.02	−1.69
1.48	1.50	+0.02	+1.35
1.69	1.71	+0.02	+1.18
		Average	−0.26
		S.D.	1.14

TABLE III

QUANTITATIVE DETERMINATION OF TIN IN TIN SULPHIDE

Weight (mg)	*Found (mg)*	*Error (mg)*	*Relative error (%)*
4.08	4.05	−0.03	−0.74
6.22	6.18	−0.04	−0.64
3.67	3.69	+0.02	+0.54
4.88	4.84	−0.04	−0.82
5.49	5.52	+0.03	+0.55
3.84	3.80	−0.04	−1.04
		Average	−0.36
		S.D.	0.71

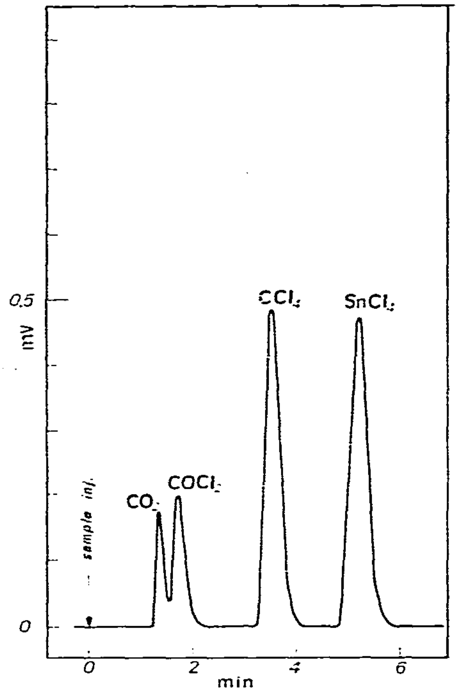

Fig. 3. Gas–liquid chromatogram for the chlorination of tin(IV) oxide with carbon tetrachloride. Chromatographic conditions as in Fig. 1 except for carrier gas (nitrogen) flow-rate, 38 ml/min.

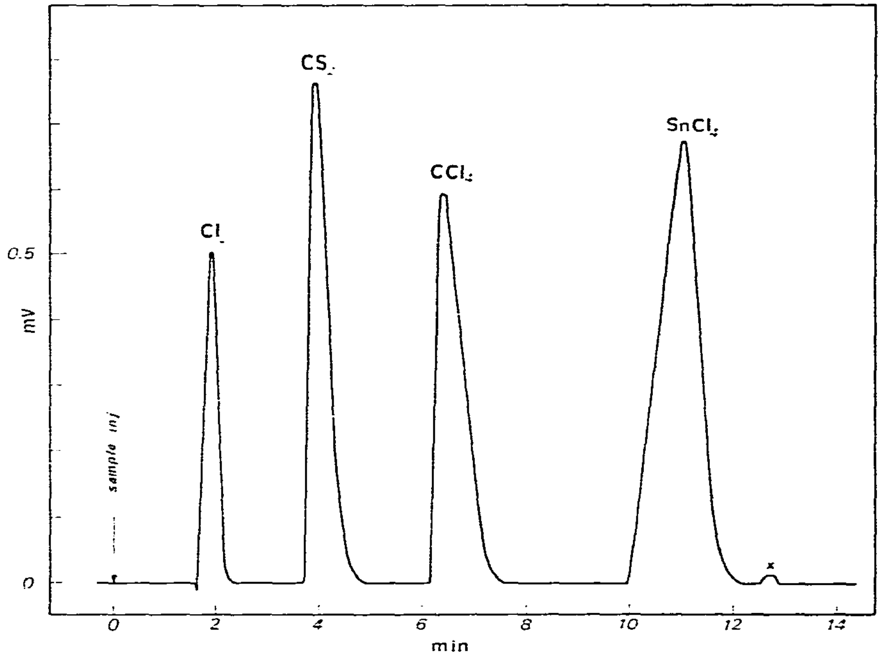

Fig. 4. Gas–liquid chromatogram for the chlorination of tin sulphide with carbon tetrachloride. Chromatographic conditions as in Fig. 3.

From a thorough study of the chlorination reaction of tin oxygen- and sulphur-containing compounds and alloys with CCl_4, it has been found that a number of stable compounds are produced, such as CO_2, $COCl_2$, CS_2, Cl_2, C, while others (C_2Cl_6, C_6Cl_6) result from the thermal decomposition of CCl_4, hexachloroethane being predominant. The peak x, in the chromatograms of Figs. 2 and 4, is not attributed to a compound containing Sn. Attempts are on the way for the identification of the nature of this peak. The presence of these compounds does not constitute the disadvantage of the proposed method since their peaks in the subsequent chromatogram do not affect the quantitative measurement of the tin tetrachloride peak, their retention times being considerably different from that of $SnCl_4$. The $SnCl_4$ peak area is measured through the trapezoid construction, and the calibration graphs used are linear within the range of 0.5–10 mg Sn. The detector sensitivity throughout the determination (applying a filament current of 150 mA) was within the range of 300–1000 mV·ml/mg. The baseline drift during 24 h of continuous operation was negligible (less than 0.01 mV for 1 mV full scale deflection of the recorder).

TABLE IV

CHLORINATION CONDITIONS OF VARIOUS TIN SAMPLES

Compound	*CCl_4 added (μl/mg of sample)*	*Chlorination time (min) at 575°*
Phosphor bronze	0.5	10
Tin–lead alloy	0.5	10
Wood'sche alloy	0.6	8
Tin–lead–antimony alloy	1.0	10
Babbit alloy	0.5	8
Tin oxide	1.3	15
Tin sulphide	1.1	15
Tin ore	1.3	25

From the results obtained (Table I, II, III, V) it is concluded that the conversion of tin into its volatile tetrachloride by reaction with carbon tetrachloride, as described above, is quantitative. The proposed method is precise, accurate and selective over a wide range of tin (1% up to 99%) giving a relative error <0.36% and a relative standard deviation <0.71%.

No interference from other elements or compounds has been observed. The method is sufficiently sensitive to detect 10^{-5} g Sn in the sample and gives quantitative results for samples containing as much as $1.5 \cdot 10^{-3}$ g Sn.

These characteristics of the proposed method appear very attractive when compared to other existing methods for the quantitative determination of tin.

TABLE V

QUANTITATIVE DETERMINATION OF TIN IN TIN ORE

Sample weight (mg)	28–50
No. of determinations	10
Tin (%)	
Present	5.75
Found	5.64
S.D.	0.002

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