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Gas-Chromatographic Separation of Inorganic Chlorides and its Application to Metal Analysis: I. Qualitative and Quantitative Aspects of the Gas-Chromatographic Separation Procedure

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Gas-Chromatographic Separation of Inorganic Chlorides and Its Application to Metal Analysis:

I. Qualitative and Quantitative Aspects of the Gas-Chromatographic Separation Procedure

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Summary

A study has been made of the potentialities of gas chromatography as a tool for the analysis of metals and alloys. As is demonstrated in the present paper, gas chromatography can be used for the separation and the quantitative determination of inorganic chlorides.

With proper adaptation of the apparatus and technique to the reactivity of these compounds, satisfactory chromatograms were obtained, showing good peak symmetry, stable baselines, and absence of artefact peaks.

Of nineteen substances studied, having boiling points between 50 and 250°C, all but a few were determined accurately in mixtures. The exceptions are the very unstable vanadium tetrachloride and antimony pentachloride (dissociating readily even at relatively low temperatures) as well as an oxychloride of molybdenum, of which the identity was uncertain.

A number of determinations carried out on a mixture of the tetrachlorides of silicon and tin under various conditions showed a good reproducibility: standard deviations of 0.2 to 0.6 wt % were found.

The analysis of metals and alloys will be reported in a subsequent paper.

INTRODUCTION

Contrary to the widespread use of gas chromatography in the organic field, there has been, in practice, little incentive to apply it to inorganic analysis, notwithstanding the fact that the interesting possibilities of this technique in the latter field were recognized early by its founder (*1*). A few exceptions are the analysis of permanent gases and perhaps also that of boron, silicon, and germanium hydrides as well as some metal-organic compounds (e.g., alkylsilanes and lead alkyls).*

The main reason for this lack of acceptance is perhaps that inorganic compounds are, in general, much more reactive than organic substances. By virtue of this, the former are readily amenable to classical chemical analysis, whereas, for the same reason, quantitative gas-chromatographic analysis becomes less easy. By contrast, the relative inertness of most organic compounds and/or the fact that they react in a similar way limit the possibilities of chemical analysis, whereas detailed analyses are easily obtained by gas chromatography. It is of interest to note that the more important examples of inorganic applications of gas chromatography mentioned above refer to cases where wet chemical methods of analysis also fail, because of the inertness or chemical similarity of the compounds involved.

It may seem, therefore, that there is little justification for applying gas chromatography to problems such as metal analysis, where the elements exhibit sufficient differences in chemical behavior to allow the application of chemical methods of analysis, now well established. However, gas-chromatographic techniques combine such important features as speed, sensitivity, selectivity, simplicity of manual operations required, adaptability to automation, etc. These features were considered sufficiently attractive to warrant closer study of the potentialities of metal analysis via this route.

CHOICE OF METAL DERIVATIVES

Apart from the metals themselves, which have very high boiling points with a few exceptions (e.g., mercury), several classes of derivatives may be considered, e.g., halides, chelates, hydrides, alkyls, and carbonyls. Unfortunately, there is no class of which all members are sufficiently volatile at temperatures at which they are reasonably stable. In this respect, the halides offer the widest range of possibilities, much wider in fact than that covered

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* Applications of gas chromatography in the inorganic field have been reviewed by Tadmor (2) and Anvaer and Okhotnikov (3).

by the chelates (acetonyl acetates and their fluorinated analogues), on which interest has so far primarily centered because of their relative inertness (*4–8*).

Accordingly, we have chosen the halides, more specifically the chlorides, for our study. Another motive underlying our choice is the consideration that there may be a possibility of converting metals and perhaps also oxides directly into the halogen derivatives, thus avoiding the wet chemical route of analysis altogether.

The present paper deals with the gas-chromatographic separation and the quantitative determination of inorganic chlorides with boiling points up to about 250°C. The analysis of metal and alloy samples will be published separately.

GAS CHROMATOGRAPHY OF VOLATILE INORGANIC CHLORIDES

Freiser (9) studied the separation of the tetrachlorides of tin and titanium, using a commercial GLC instrument with katharometer detector. The copper columns were filled with *n*-hexadecane on red Chromosorb, and the operating temperature was about 100°C.

This study was extended by Keller and Freiser (*10*) by including the pentachlorides of niobium and tantalum and the use of somewhat less volatile stationary phases (*n*-octadecane and squalane) at temperatures of 150 to 200°C. In another paper (*11*) Keller reported the use of Apiezon T, paraffin wax, and silicone oil as stationary liquids on red Chromosorb as a support in copper columns. The same solutes were studied at 100 to 200°C.

Although the above authors have shown that the four chlorides mentioned can be separated, their work is more of a qualitative nature, as quantitative data are not given. Studying the chromatograms shown by Keller (*11*), we conclude from the presence of shoulders, tails, and artefact peaks that decomposition of solutes must have occurred to a large extent within the column. This conclusion is also supported by the very considerable effect of even slight changes in flow rate (variation of residence time in column) on concentration profiles.

Juvet and Wachi (*12*) used a eutectic mixture of $BiCl_3$ and $PbCl_2$ on Sil-O-Cel C 22 firebrick for a gas chromatographic separation at 240°C of titanium tetrachloride and antimony trichloride.

They conducted their experiments in a glass apparatus. The chromatogram shown by these authors exhibits a pronounced baseline instability, notwithstanding that the katharometer was evidently used at a not very high sensitivity level, since a large sample (35 μl) was injected. No data are given which permit us to assess the quantitative aspects of this separation.

Abe (*13*) studied qualitatively the separation of the volatile chlorides of B, Si, and P ($SiHCl_3$, $SiCl_4$, BCl_3, and PCl_3) on stationary phases such as dioctyl phthalate, tritolyl phosphate, and silicone oils. Quantitative results are claimed for a mixture of $SiHCl_3$ and $SiCl_4$ on silicone oil as a stationary phase.

Tadmor (*2,14*), however, found silicone products to be unsuitable as stationary phases for the quantitative analysis of metal halides. Well-defined peaks attributable to reaction products were obtained when analyzing $GeCl_4$, $SnCl_4$, and $AsCl_3$ with silicone grease as a stationary phase.

In a later paper (*15*) (which appeared after completion of the present study) Tadmor reported on the use of bare Sil-O-Cel C 22 firebrick as a separating medium for $GeCl_4$, $SnCl_4$, and $AsCl_3$ at 100°C. With columns pretreated by injection of Cl^{36}-labeled HCl, rapid isotopic exchange occurred with solutes in the columns, thus permitting the detection of the eluted products by means of a continuous β counter. With the uncoated support the adsorptivities of the solutes differed markedly, but since peaks were broad and exhibited tailing, the separation was incomplete. Better separation was obtained by coating the support with 1% nitrobenzene. The chromatograms shown exhibit peak shapes which are considerably distorted (fronting, tailing, and shoulders). The author is well aware of the incompleteness of the recovery and attributes the losses to hydrolysis occurring within the column.

Wilke et al. (*16*) recently reported on the gas-chromatographic analysis of the tetrachlorides of silicon, tin, and titanium with a view to determining impurities of the above products. They used a commercial instrument with katharometer detector. Nitrobenzene, silicone oil, and Apiezon N were used as stationary phases at about 100°C on diatomaceous firebrick supports (Sterchamol, Diaphorit). They stated that to obtain separate peaks for $SiCl_4$ and $TiCl_4$ it is necessary to pretreat the columns by a large series of injections of $TiCl_4$. Although a complete separation is reported with a column thus treated, the peaks still exhibit considerable tailing, as is evident from the chromatograms shown. No proof is given of complete recovery of solutes from the column.

INTERACTION BETWEEN COLUMN MATERIALS AND SOLUTES

Since in analytical gas chromatography, milligram or submilligram amounts of sample are brought into contact with at least a thousandfold amount of column materials, it is evident that when reactive substances are involved, the inertness of column materials has to meet severe demands.

Previous experience with the quantitative determination of reactive halogen compounds (such as HCl, HBr, HI, Cl_2, Br_2, ICl, NOCl, $COCl_2$, BCl_3, etc.) in gases* had shown that the use of conventional column materials (metal, organic liquids except completely halogenated products, and diatomaceous supports) is not allowed if quantitative results are aimed at.

The lack of inertness of metals such as copper and stainless steel is perhaps best illustrated by the ready attack of these by chlorinating agents, as experienced in our study on the preparation of metal derivatives. Further proof of the unsuitability of, for instance, copper is the violent reaction observed between it and $SbCl_5$, both in the liquid and in the gas phase. A short bed of copper turnings has been found to retain $SbCl_5$ completely from a gas stream, reducing the chloride with probable formation of an antimonide.

Diatomaceous supports are unsuitable for the present purpose because of their adsorptive properties. For example, large amounts of HCl are almost irreversibly adsorbed by Sil-O-Cel C 22 (Chromosorb R or P). The experiments by Tadmor (*14,15*) (referred to before) also serve to illustrate the great adsorption affinity of these supports for metal halides. Even the white diatomaceous supports, which are usually regarded as being less adsorptive than the above-mentioned red ones, are unsuitable, because of the numerous metallic impurities which may react (Tables 1 and 2). From Table 2, which presents some results of emission spectroscopic analysis, it can be seen that even rigorous acid treatment fails to remove these impurities completely. On the other hand, the partial removal suggests that they are not harmless.

* Unpublished work.

TABLE 1

Composition of Typical Diatomaceous Supports[a]

Constituent	Chromosorb P, wt %	Chromosorb W, wt %
SiO_2	90.6	88.9
Al_2O_3	4.4	4.0
Fe_2O_3	1.6	1.6
TiO_2	0.3	0.2
P_2O_5	0.2	0.2
CaO	0.8	0.6
MgO	0.7	0.6
$Na_2O + K_2O$	0.5	3.6
Moisture + ignition loss	0.3	0.3

[a] Data supplied by Johns-Manville Corporation (*17*).

TABLE 2

Effect of Hydrochloric Acid Treatment[a] on the Impurity Content of Celite 545

Impurity	Before treatment, wt %	After treatment, wt %
Na	2.4	2.2
Al	1.4	1.2
Fe	1.2	1.1
K	0.90	0.87
Ca	0.32	0.26
Mg	0.28	0.23
Ti	0.13	0.088
B	0.070	0.054
Ni	0.031	0.022
Ba	0.015	0.015
V	0.015	0.0098
Cr	0.0064	0.0052
Cu	0.0039	0.0022
Sr	0.0039	0.0027

[a] Treatment consisted in repeated leaching of support with concentrated hydrochloric acid at 100°C for several days until the filtrate was practically free of iron, as evidenced by a negative thiocyanate test.

Some of the chlorides are active chlorinating agents (e.g., SCl_2, $SbCl_5$) and, moreover, free chlorine may be present in the sample (for instance, when the chlorides have been prepared by chlorination). The stationary liquid should, therefore, be at least resistant to chlorination. This condition is not met by the organic stationary phases employed by the authors mentioned in the preceding section. As an illustration, Fig. 1 shows how considerable amounts of HCl are formed when Cl_2 is contacted with silicone grease, even at temperatures as low as room temperature.

CHOICE OF COLUMN MATERIALS AND DETECTION SYSTEM

A gas density balance was chosen as detector, with regard to the following considerations:

1. The relative response factors are accurately predictable.
2. Nitrogen can be used as a cheap inert carrier gas.
3. Since all chlorides have a molecular weight differing appreciably from nitrogen, the sensitivity is reasonably high.
4. The sensitive parts do not come into contact with corrosive samples, thus reducing the chances of drifts in zero signal and sensitivity and promoting longer trouble-free operation.

The first feature is perhaps the most important one, since it permits checking the quantitative recovery of solutes. With the size of liquid samples only approximately known (as is usual in gas chromatography and perhaps even more so when injecting microliter quantities of reactive substances), empirical calibration techniques are commonly used for such devices as a katharometer detector. This procedure does not yield information on the occurrence of losses in the column. Any loss that may occur will be hidden in the empirically determined response factor. Consistency of results only indicates that, with operating variables kept constant, the extent to which these losses occur is reproducible. On the other hand, with response factors accurately predictable, it is possible to compare the peak size of the suspected solute with that of a perfectly inert solute obtained by analyzing a known mixture of both, thus determining the recovery of the first.

The stationary liquid chosen is a trifluoromonochloroethylene polymer (Kel-F 40 polymer wax, obtained from Minnesota Mining & Manufacturing Co.). As can be seen from Fig. 1, this material is sufficiently inert toward chlorine. Columns filled with it proved to be stable up to about 150° C (short operation is possible at 175°C).

As an inert support, only polytetrafluoroethylene polymers have been considered. The products examined included Fluon Powder (Grade 1, Imperial Chemical Industries Ltd.), Fluoro-

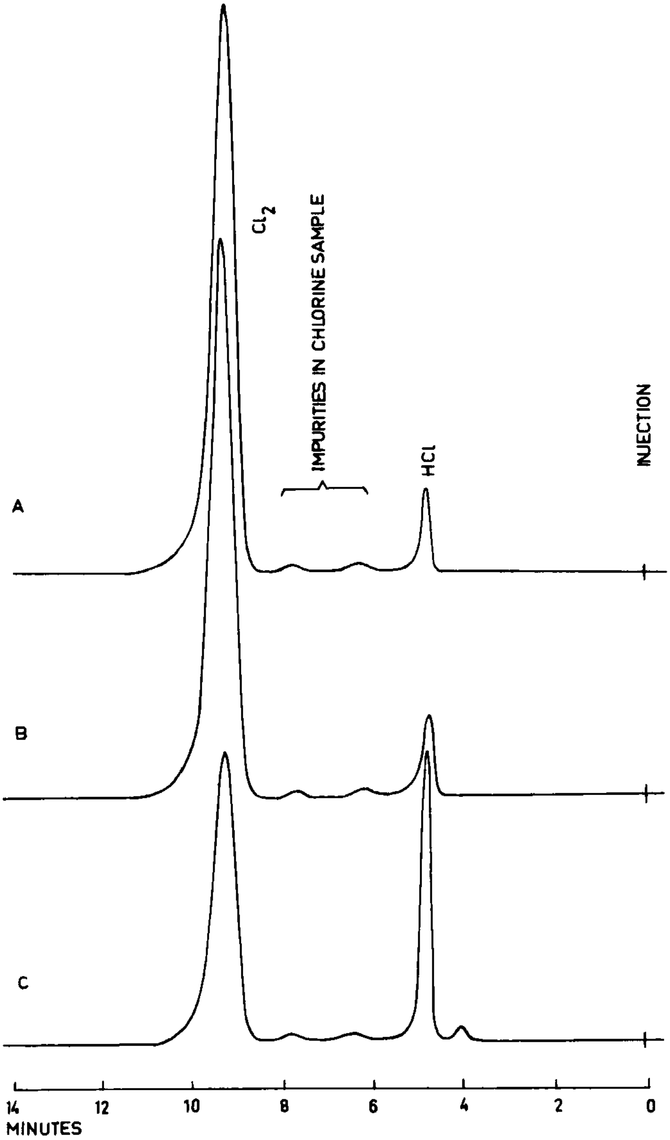


FIG. 1. Reaction of chlorine with stationary liquids. A, chromatogram of original chlorine sample; B, chromatogram of chlorine sample contacted with Kel-F polymer wax (0.7 g of gaseous chlorine contacted with approx. 2 g of wax for 16 hr at 20°C); C, chromatogram of chlorine sample contacted with silicone grease (same conditions as B).

(*Continued on facing page.*)

pack 80 (The Fluorocarbon Company, Fullerton, Calif.) and Haloport F (F & M Scientific Co., Avondale, Pa.). The last material was chosen, because it proved to give the best over-all performance (ease of handling, column plate height, and column permeability). Glass was chosen as the column material.

APPARATUS AND TECHNIQUE

Apparatus

A schematic diagram is given in Fig. 2. The carrier gas was nitrogen, containing some argon and traces of oxygen (< 10 ppm v/v) as main impurities. It was passed at high pressure over dry silica gel to remove moisture and organic vapors, if present. After expansion to the working pressure it was dried over a large-

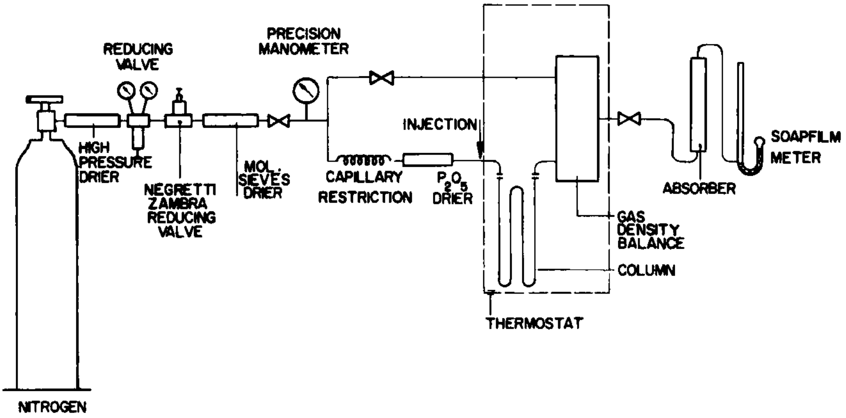


FIG. 2. Schematic diagram of apparatus.

Conditions of analysis:

Column 6.50 m × 8 mm I.D. glass column filled with approx. 15 wt % Kel-F 10 on Haloport F.

Column temperature: 20°C

Carrier gas: He

Flow: approx. 5 liters/hr

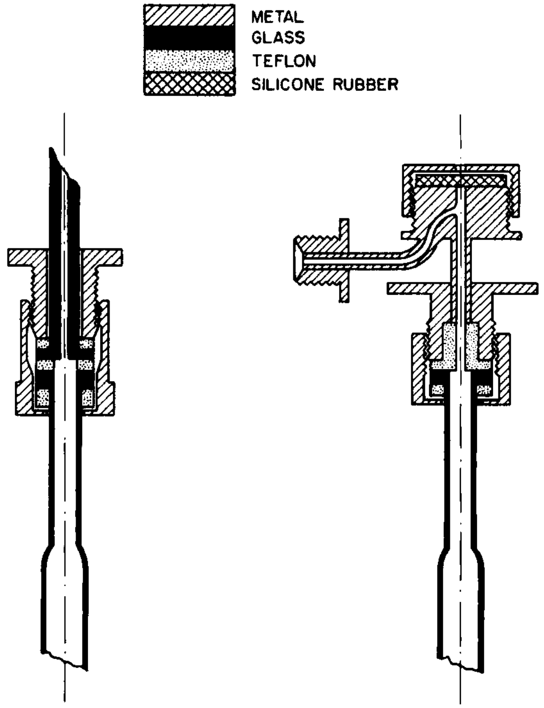
Detector: Monel katharometer with Teflon-clad tungsten filaments

Sample size: 1.24 ml of gas

Attenuation factor: 50

capacity drier (filled with activated Linde 5 A molecular sieves). As a final precaution against traces of moisture entering the column, a drier containing powdered P_2O_5 was situated outside the thermostat just before the sample inlet.

Figure 3 shows details of the injection port and the connection of glass columns to, for instance, other columns or the detector. As can be seen, the only materials coming into contact with the sample are glass and Teflon.



A COLUMN CONNECTION B SAMPLE INJECTION PORT

FIG. 3. Details of apparatus.

The columns were W-shaped glass columns of 8 mm I.D. (mostly of 2 m length) kept in an air thermostat (accuracy of temperature regulation ±0.5°C). Column filling consisted of 15 wt % Kel-F 40 on Haloport F (30/80 mesh).*

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* Some care is needed in its preparation to prevent agglomeration of particles.

The detector used was a gas density balance of the type described by Nerheim (*18*) and constructed from Monel* (Model 091 of Gow Mac Instrument Co., Madison, N.J.). Sensing elements were Teflon-coated tungsten filaments (Gow Mac Type 9225), connected in a Wheatstone-bridge arrangement with 100-ohm resistors. Bridge current was 150 ma. The auxiliary electrical part was of conventional design and needs no special description.

The combined reference and column effluent streams were passed through a tower filled with moistened KOH pellets to prevent escape of chlorides into the working room.

Column flow and the combined flow were measured with a soap-film flow meter. Column flow was varied between 2.0 and 4.2 liters/hr; reference flow ranged between 3.0 and 5.1 liters/hr.

Reagents

Of the inorganic chlorides listed in Table 3, most had an estimated purity exceeding 98% (impurities being mainly products of hydrolysis). Products, which had a lower purity, were:

Sulfur Dichloride. Samples prepared by chlorination of pure S_2Cl_2 with traces of ferric chloride as a catalyst contained some undissolved chlorine and unreacted S_2Cl_2 as impurities. The amount of the latter (approx. 10 wt %) was determined by gas chromatography at relatively low temperatures (20 to 30°C), using a short (50 cm) column filled with Kel-F 10 on Haloport F.†

Antimony Pentachloride. The purity of the commercial sample which contained free chlorine (possibly as a result of partial dissociation) was unknown.

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* Although a gas density balance can be made of glass, it was considered that the inertness of this alloy should be sufficient at the working temperatures of 150°C and below, having regard to the short contact times (residence time of the order of seconds) and to the high dilution of the solutes with carrier gas after the chromatographic process.

† The possibility of the purity figures thus obtained reflecting a partial dissociation of SCl_2 in the column was rejected, since at the low temperatures involved SCl_2 is reasonably stable. The chromatograms showed well-defined symmetrical peaks for Cl_2, SCl_2, and S_2Cl_2, and the results were accurately reproducible, regardless of temperature variation, within the stated limits and wide variations in flow rate and sample size. Consistent results were also obtained when samples were mixed and analyzed as mixtures.

TABLE 3

Relative Retention Times and k' Values of Inorganic Chlorides[a]

			Relative retention time				K'			
Element	Substance	Boiling point, °C	75°C	100°C	125°C	150°C	75°C	100°C	125°C	150°C
C	CCl_4	76.7	100	100	100	100	4.78	2.62	1.58	0.99
Si	$SiCl_4$	57.0	54	55	56	57	2.58	1.44	0.89	0.57
P	PCl_3	76	78	79	80		3.71	2.08	1.27	
	$POCl_3$	105.3	227	189	172		10.8	4.96	2.71	
S	SCl_2	59	42	44	49		1.99	1.15	0.78	
	S_2Cl_2	138	264	233	216		12.6	6.10	3.41	
	$SOCl_2$	75.7	79	76	74		3.75	1.98	1.17	
	SO_2Cl_2	69.2	85	85	85		4.07	2.23	1.35	
Ti	$TiCl_4$	135.8	379	313	287		18.1	8.20	4.53	
V	VCl_4	152[b]		445	386	319		11.7	6.10	3.16
	$VOCl_3$	127		260	222	209		6.97	3.81	2.07
Cr	CrO_2Cl_2	117	251	220	204		12.0	5.77	3.23	
Ga	Ga_2Cl_6	200				755				7.47
Ge	$GeCl_4$	83.1	104	100	99		4.99	2.62	1.57	
As	$AsCl_3$	130	227	202	189	174	10.8	5.29	2.98	1.72
Mo	MoO_2Cl_2[c]	Unknown		285	248	218		7.47	3.90	2.16
Sn	$SnCl_4$	113	183	161	150	139	8.73	4.23	2.37	1.38
Sb	$SbCl_3$	221		666	546	460		17.5	8.64	4.56
	$SbCl_5$	[d]		1180	886	683		31.0	14.0	6.76

[a] Column: 2.00 m × 8 mm I.D. glass column filled with 15 wt % Kel-F 40 on Haloport-F 30/80 mesh. Reference substance: carbon tetrachloride.

[b] With decomposition.

[c] Identity not certain.

[d] Decomposes. Boiling point at reduced pressure: 76.5°C/21 mm Hg.

Vanadium Tetrachloride. A product of unknown purity, also containing free chlorine, was obtained commercially in a small steel cylinder (Stauffer Chemical Co., New York).

Besides the above products, which were available in larger quantities, a few chlorides were produced by in-situ chlorination on a microscale, using a technique developed for the conversion of metals.[*] These chlorides were:

Vanadium Tetrachloride. Prepared by chlorination of metallic vanadium (of approx. 95% purity) at 700°C under anhydrous and oxygen-free conditions (*19*).

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[*] To be published.

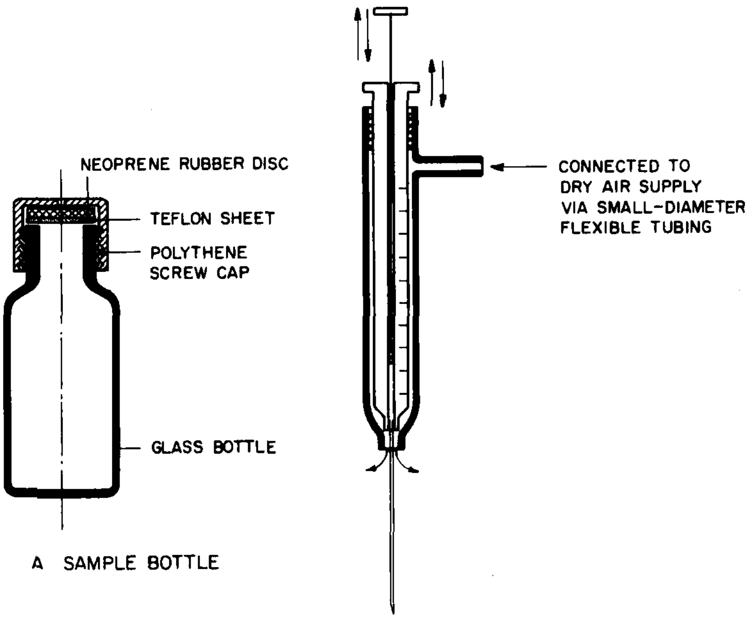
Vanadium Oxytrichloride. Prepared by chlorination of the metal at 700°C in the presence of oxygen, by reaction (*19*) of Cl_2 with V_2O_5 at 900°C, or by heating V_2O_5 with Al_2Cl_6 (*20*) (purity of both V_2O_5 and vanadium approx. 95%).

Molybdenum Oxychloride. Obtained by chlorination of the metal in the presence of oxygen at 700 to 900°C. The identity of this product (possibly MoO_2Cl_2) is not certain.

Preparation of Test Mixtures and Techniques of Injection

Mixtures of known composition were prepared by adding liquid products by means of hypodermic syringes to previously dried sample bottles provided with a septum [see Fig. 4(a)]. Solids ($SbCl_3$, Ga_2Cl_6) were added as such in a dry atmosphere. The exact amount added was determined by weighing.

For the injection of samples into the column several techniques were tested. One found to be suitable and most convenient con-



A SAMPLE BOTTLE

B MICRO SYRINGE
WITH DRY-AIR-PURGED SHEATH

FIG. 4. Sampling accessories.

sists in piercing the sample bottle septum with the syringe needle until its tip is in the liquid, then filling and emptying the syringe several times, adjusting the volume, and withdrawing the needle until its tip is just above the liquid. The plunger is then moved backward, thus filling the needle with moisture-free gas. Finally the syringe is withdrawn from the bottle and the sample injected immediately.

Since moisture from the ambient air can only[1] reach the sample by diffusion through the long narrow needle, and as the needle tip is only exposed to the atmosphere for a second at most, loss of sample is negligible.

After each injection the syringe is cleaned with dry carbon tetrachloride. Hamilton microsyringes of 10-μl capacity of the normal type, as well as gas-tight syringes with a Teflon plunger of 50-μl capacity, were used primarily.

Several refinements to the above technique were tried but found to give essentially the same results. For instance, no advantage attached to keeping syringes permanently free of adsorbed moisture by a permanent filling with acetyl chloride when they were not in use. Nor was a significant improvement observed when the needle tip was closed by a sliding piece of silicone rubber or Teflon during transfer from sample bottle to injection port. The same was true for a technique using an improvised dry-box arrangement over the injection port or a dry-air purged sheath around the syringe, in which the needle tip could be retracted [see Fig. 4(b)].

The sample sizes ranged between 1 and 8 μl of liquid.

RESULTS AND DISCUSSION

Qualitative Aspects

Symmetry of Peaks. Figures 5 to 14 are examples of chromatograms obtained. As can be seen, the peak shape is quite satisfactory for nearly all the solutes examined. Apart from the few exceptions to be discussed below, solutes gave symmetrical peak with little, if any, tailing. Besides small peaks attributable to HCl (present as impurity in the product and from the gas phase injected) no artefact peaks were observed at all. Baselines were perfectly stable.

$TiCl_4$ and Ga_2Cl_6 were exceptional in giving peaks which

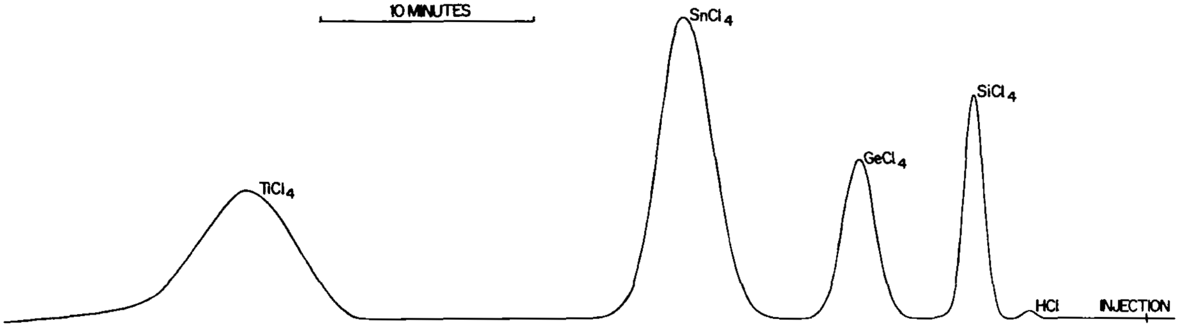


FIG. 5. Separation of the tetrachlorides of silicon, germanium, tin, and titanium. Analysis carried out without addition of $TiCl_4$ to the carrier gas. Note the tailing of the $TiCl_4$ peak. Column conditions: length 2 m, temperature 75°C, flow 2.4 liters/hr.

(although of better shape than obtained by previous workers) exhibit tailing. This peak asymmetry was also reflected in the quantitative results (as will be discussed later). Tailing of these peaks was reduced by the continuous addition of the solute in question to the carrier gas (see Fig. 12).

A distorted peak shape was observed in the test on $SbCl_5$. This unstable compound will be the subject of separate discussion.

Effect of Temperature on Solute Retention. Relative retention times (with CCl_4 as a standard) for the solutes examined are listed in Table 3, together with boiling points [Bureau of Mines figures (*21*)].

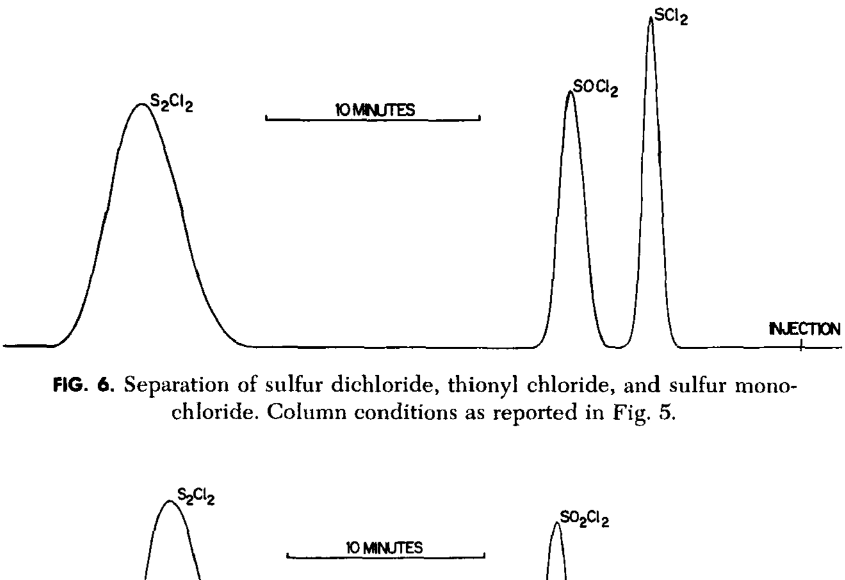


FIG. 6. Separation of sulfur dichloride, thionyl chloride, and sulfur monochloride. Column conditions as reported in Fig. 5.

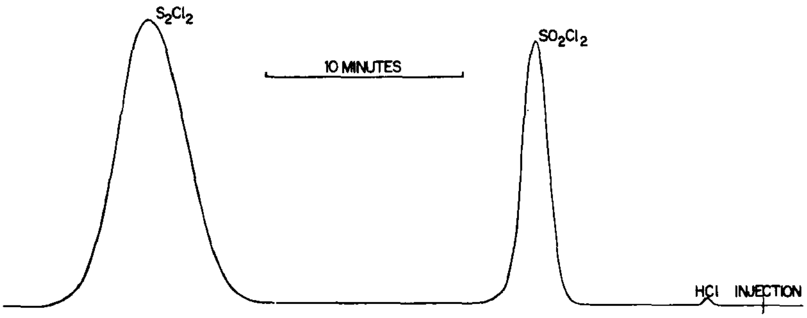


FIG. 7. Separation of sulfuryl chloride from sulfur monochloride. Column conditions as reported in Fig. 5.

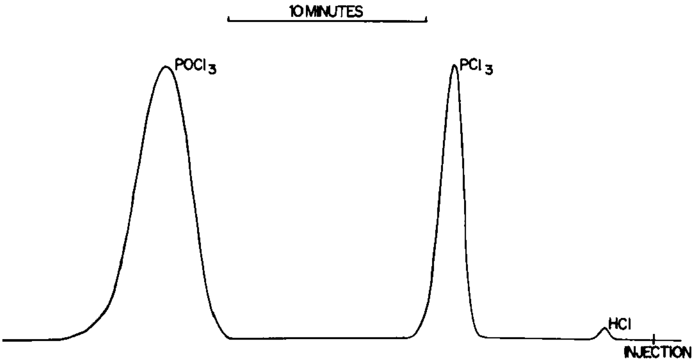


FIG. 8. Separation of phosphorus trichloride from phosphorus oxytrichloride. Column conditions as reported in Fig. 5.

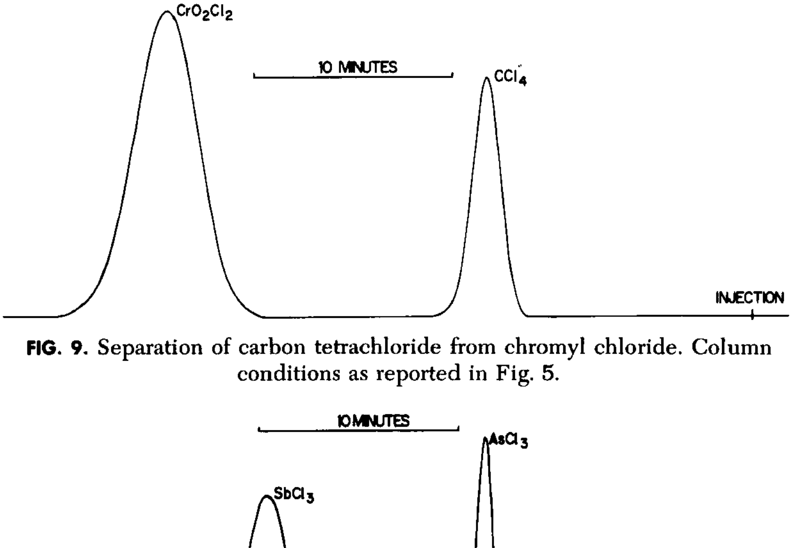


FIG. 9. Separation of carbon tetrachloride from chromyl chloride. Column conditions as reported in Fig. 5.

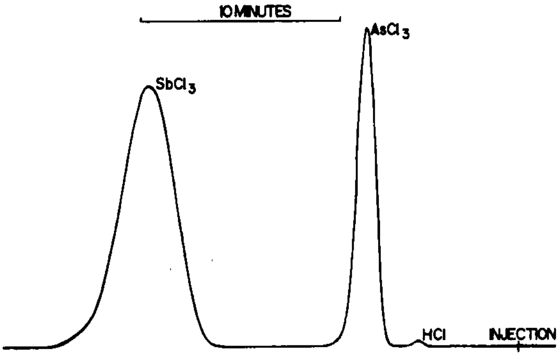


FIG. 10. Separation of the trichlorides of arsenic and antimony. Column conditions: length 2 m, temperature 125°C, flow 2.4 liters/hr.

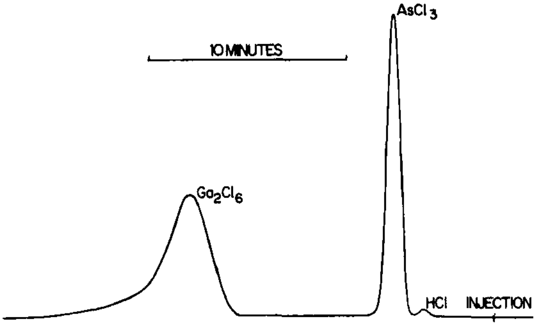


FIG. 11. Separation of the trichlorides of arsenic and gallium. Column conditions: length 2 m, temperature 150°C, flow 2.4 liters/hr.

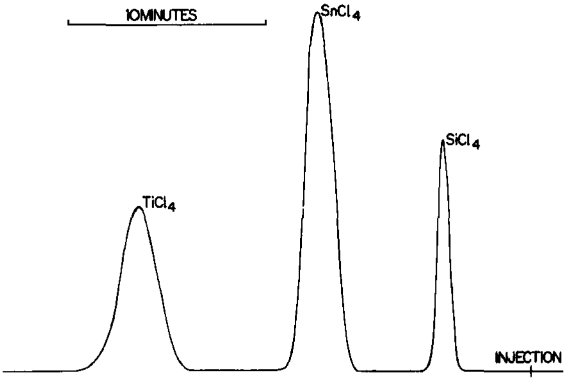


FIG. 12. Separation of the tetrachlorides of silicon, tin, and titanium. Analysis carried out with addition of about 100 ppm v/v of $TiCl_4$ to the carrier gas. Note the improved peak shape of $TiCl_4$ as compared with Fig. 5. Column conditions: length 2 m, temperature 125°C, flow 2.4 liters/hr.

Solute retention is also expressed as a modified partition coefficient (k'), defined by

$$k' = k(V_L/V_G) = (t_S - t_G)/t_G$$

where k is the true partition coefficient, V_L and V_G the volumes of liquid and gas in the column, and t_S and t_G the elution time of a solute and the gas holdup time, respectively. t_G was determined with CO_2 as a virtually nonpartitioning solute.

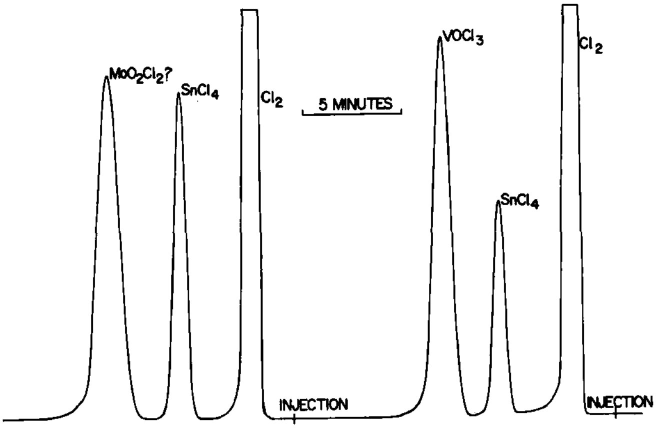


FIG. 13. Separation of tin tetrachloride from vanadium oxytrichloride and molybdenum oxychloride (chromatograms of reaction products obtained by chlorination of mixtures of tin and vanadium or tin and molybdenum in the presence of oxygen). Column conditions: length 1 m, temperature 100°C, flow approx. 2 liters/hr.

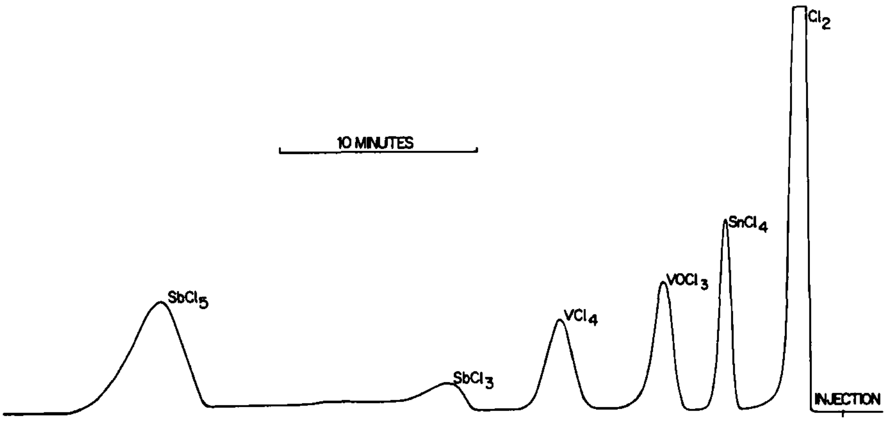


FIG. 14. Separation of reaction products obtained by chlorination of a mixture of tin, vanadium, and antimony in the presence of traces of oxygen. Note the symmetry of the VCl_4 peak and the "bridging" of the $SbCl_3$ and $SbCl_5$ peaks. Column conditions as reported in Fig. 13.

From the temperature-dependence of k' the heats of vaporization can be calculated by means of the equation

$$d(\ln k')/d(1/T) = [(\Delta H_V - \Delta H_S) - RT]/R$$

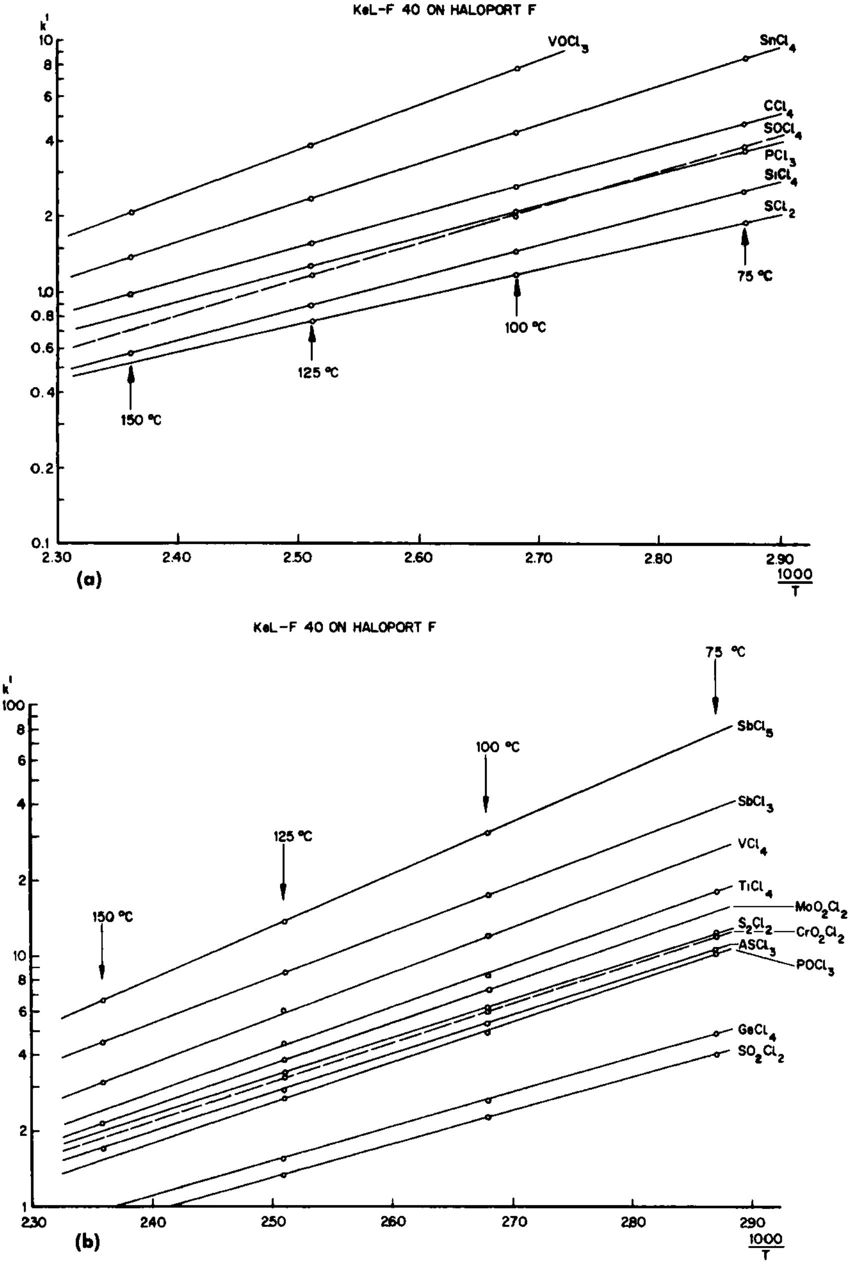


FIG. 15. Temperature dependence of the partition coefficient of inorganic chlorides.

where T is the absolute temperature, R the gas constant, and ΔH_V and ΔH_S are the heats of vaporization of the liquid solute and the partial heat of solution of solute in the stationary liquid, respectively. The difference of the latter two is the heat of vaporization of solute from the dilute solution in the stationary liquid.

As Fig. 15(a) and (b) show, the linear relationship between the logarithm of k' and the reciprocal absolute temperature predicted by the above equation is closely followed.

In Table 4 the heats of vaporization (from Kel-F solution), as determined from the gas-chromatographic experiments, have been entered against the corresponding values of the pure liquid solutes [Bureau of Mines figures (*21*)]. The two sets of values agree as to the order of magnitude (the gas-chromatographic values being generally somewhat lower).

TABLE 4

Heats of Vaporization of Inorganic Chlorides from the Liquid State and from Dilute Solutions in Kel-F 40

		Heat of vaporization, kcal/mole, at stated temperature	
Component	Boiling point, °C	From a solution of Kel-F 40 (G.C. measurements)	From the liquid state (literature data)
CCl_4	76.7	6.85	7.17
$SiCl_4$	57.0	6.49	7.0
PCl_3	76	6.51	7.28
$POCl_3$	105.3	8.17	8.21
SCl_2	59	5.76	
S_2Cl_2	138.0	7.95	8.61
$SOCl_2$	75.7	7.25	7.41
SO_2Cl_2	69.2	6.85	7.50
$TiCl_4$	135.8	8.69	8.4
VCl_4	152	9.21	9.1
$VOCl_3$	127	8.46	8.3
CrO_2Cl_2	117	8.00	8.4
$GeCl_4$	83.1	7.04	7.9
$AsCl_3$	130	8.25	7.5
MoO_2Cl_2[a]	Unknown	9.16[b]	
$SnCl_4$	113	7.94	8.3
$SbCl_3$	221	9.40	10.8
$SbCl_5$	76.5[c]	10.26	11.5

[a] Identity uncertain. [b] At 100°C. [c] At 21 mm Hg.

From the above results it can be concluded that for the reactive solutes considered, the mechanism of retention is, as it should be, a physical process of solution rather than some chemical interaction. (For the latter mechanism larger heats of transition are expected.)

Behavior of High-Melting Chlorides. Although the chlorides of aluminium, niobium, and tantalum, i.e., Al_2Cl_6 (sublimation point 180°C), $NbCl_5$ (boiling point 235°C), and $TaCl_5$ (boiling point 246°C) were originally included in the present study, they have been omitted from Table 3. At temperatures below 150°C, no well-defined peaks were obtained from these substances within a reasonable time. Such peaks could indeed be produced at higher temperatures (175°C and above), but no systematic investigation was carried out, because column bleeding became apparent at these temperatures.

It is of interest to note that Keller and Freiser (*10*), who investigated $NbCl_5$ and $TaCl_5$, used temperatures above 150°C for the elution of $NbCl_5$, while $TaCl_5$ could only be eluted at the highest operating temperature, about 200°C. (Even then elution took nearly 4 hours.)

The above results were somewhat unexpected, since $SbCl_5$ (boiling point 221°C) was eluted within reasonable time even at 100°C. The abnormal behavior of Al_2Cl_6, $NbCl_5$, and $TaCl_5$ may be associated with their high melting points (192, 210, and 211°C, respectively). Since the heats of sublimation (26.7, 20.4, and 22.7 kcal/mole, respectively) are considerably higher than the heats of vaporization from a liquid (see Table 4) vapor pressures of the solids decrease rapidly with falling temperature.

It is probable (at least for $NbCl_5$ and $TaCl_5$) that below 150°C the minimum vapor pressure at the column entrance which is required to obtain well-defined peaks exceeded the saturation pressure of the solute.

Concentration Profiles for Dissociating Compounds. VCl_4 and $SbCl_5$ are known to dissociate easily into the respective trichlorides and chlorine. Dissociation of VCl_4 when refluxed is used as a convenient means for the preparation of VCl_3 (22). Dissociation of $SbCl_5$ at temperatures below its atmospheric boiling point is the reason why the latter is unknown. According to the literature, VCl_4 and $SbCl_5$ dissociate slowly even on standing at room temperature, when not in a closed vessel under chlorine pressure (*23,24*). In view of the above, it is hardly to be expected that VCl_4 and $SbCl_5$ can pass through a gas-chromatographic column unscathed. It is, therefore, rather surprising that they gave recognizable and reproducible peaks at all. As can be seen from Fig. 14, the peak of VCl_4 is even quite symmetrical and does not suggest any decomposition. Nevertheless, this must have occurred, since the peaks were found to be smaller than theoretical. Besides, evidence was obtained of deposition of vanadium compounds in the column: After a series of VCl_4 samples had passed through the column it proved possible to generate VCl_4 by injecting chlorine.

The phenomena described above can be understood by considering that the trichloride (which is probably formed) is involatile. It remains in the column and is reconverted partially by chlorine passing over it. The dissociation of VCl_4 into VCl_3 is known to be reversible, leading to an equilibrium (*23*). Since the chlorine liberated by dissociation of VCl_4 comes off the column gradually, and as the sensitivity of the detector for chlorine is low, no additional chlorine peak is seen in the chromatograms.

The behavior of VCl_4 demonstrates strikingly that we may not regard a symmetrical peak and the absence of artefact peaks as proofs of the soundness of the gas-chromatographic procedure, as is too often (tacitly) done.

As follows from Fig. 14, antimony pentachloride behaves differently, because its decomposition product is volatile. It is seen that the shape of the $SbCl_3$ peak is distorted, the signal failing to return to the baseline between the two antimony chloride peaks. This might suggest decomposition of $SbCl_3$, but such is not the case, as follows from Fig. 10. The "bridging" of the two peaks may be explained by the gradual generation of $SbCl_3$ from $SbCl_5$ during the time the latter is subjected to the chromatographic process, in addition to the amount of $SbCl_3$ already present in the sample.

Quantitative Aspects

Detector Response. Previous experiments with inert solutes (hydrocarbons, freons) confirmed that the relative molar response factors of the gas density balance are accurately proportional to the difference in molecular weight between solute and carrier gas. Response factors calculated from molecular weights agreed within about 2% with experimental ones, in accordance with the findings of Phillips and Timms (25).

With hydrocarbons as solutes, the detector proved to be linear within a range of about 1:500. The sample sizes used in the present investigation were chosen accordingly.

Recovery of Inorganic Chlorides from the Column. Except for the dissociating chlorides (VCl_4, $SbCl_5$) and molybdenum oxychloride (of which the identity is uncertain), recovery from the column was checked for all solutes listed in Table 3. Test mixtures involving all solutes but $VOCl_3$ were prepared and analyzed. Quantitative evaluation of chromatograms was done on the basis of peak areas with theoretically calculated response factors. Recovery was found to be complete (within a few per cent) for all solutes tested, except for $TiCl_4$ and Ga_2Cl_6 (to be discussed below).

As additional proof of the absence of serious losses of the former solutes, it may be mentioned that variation of flow rate and temperature did not produce any observable effect other than the ones to be expected—change in elution times, degree of separation, and absolute detector sensitivity.

With $SiCl_4$ and $SnCl_4$ we also examined the possible effects of variation of sample size and repetitive injections. Such effects proved to be almost nonexistent (see Tables 5 and 6).

Recovery of $TiCl_4$ and Ga_2Cl_6. The results for these two solutes, which had already been distinguished by peak asymmetry, were consistently low (50 to 97% of the theoretical). Since both are extremely sensitive to moisture, it was at first suspected that some drolysis had occurred during sample handling. However, additional measures taken to diminish the chances of such hydrolysis (see "Preparation of Test Mixtures and Techniques of Injection," above) failed to effect the desired improvement, showing that the injection procedure was not to blame.

The possibility of residual moisture in the carrier gas reacting with the solutes was then considered and ruled out, since the amount that could possibly have entered the column within the analysis period seems to be much too small to have caused the losses observed. As low results were also obtained with columns which had been used for a considerable time (while continuously purged with dry gas), it seemed unlikely that wet columns

TABLE 5

Absence of Sample-Size Effect in the Determination of $SiCl_4$ and $SnCl_4$ in Mixtures (Analysis at 75°C)

Sample size, μl	$SiCl_4$, wt %	$SnCl_4$, wt %
1	12.7	38.8
1.5	12.6	37.9
2	12.6	38.2
3	12.7	37.9
Theoretical	12.4	38.2

TABLE 6

Absence of Injection-Sequence Effect in the Determination of $SiCl_4$ and $SnCl_4$ in Mixtures (Analysis at 75°C)

Injection No.	$SiCl_4$, wt %	$SnCl_4$, wt %
1	12.7	38.2
2	12.8	38.2
3	13.3	39.3
4	12.8	38.0
5	12.6	38.3
6	12.7	38.3
Theoretical	12.4	38.2

should be the source of trouble. Nor does irreversible hydrolysis of the chlorides in the column (yielding, for instance, involatile oxides) satisfactorily account for the tailing of the peaks. Moreover, such an irreversible loss of solute could have been remedied by repeated injections of the solute, thus exhausting the inventory of moisture in the column. As is shown in Table 7, repetitive injections indeed give successively higher recovery figures, but the improvement was found to be temporary. After the column had been purged with carrier gas for half a day or so, the situation was nearly the same as before the injections.

The phenomena seem to be compatible with a strong adsorption or a chemisorption which is to a certain extent reversible, on the analogy of the well-known behavior of strongly polar substances (water) in GLC columns. This means that the "losses" of solute are actually "hidden" in a tail of the peak.

If such an adsorption is attributable to the polar inner surface of the glass column, it may well be possible to eliminate the effect by the use of Teflon tubes. We did not investigate this possibility, as we succeeded in reducing the tailing in another way, by adding traces of the compound in question to the carrier gas. A convenient means of doing this is by using a diffusion capillary (in the case of $TiCl_4$) or by passing carrier gas over a bed of solute at a predetermined temperature (method employed with solid Ga_2Cl_6).

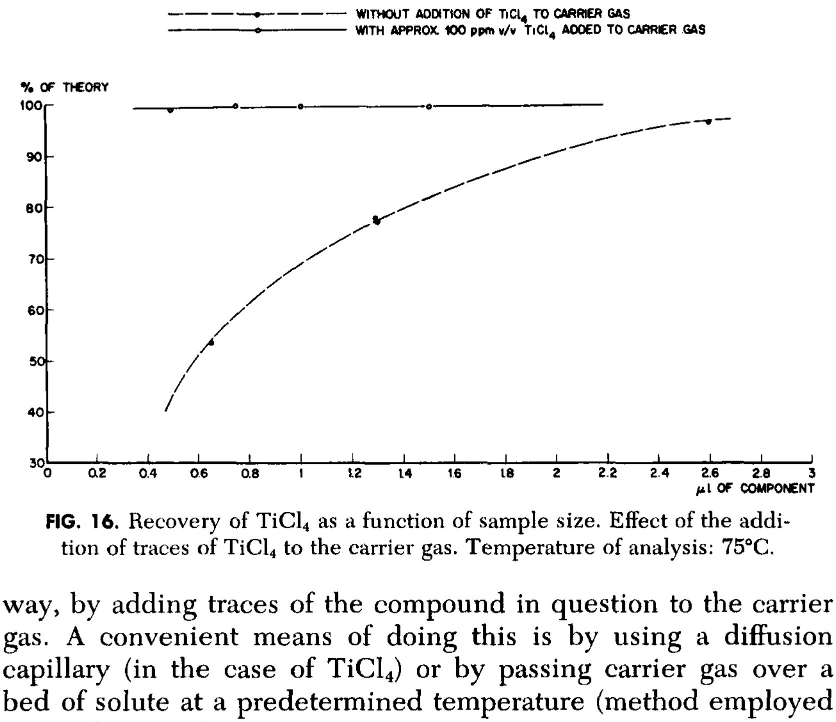


FIG. 16. Recovery of $TiCl_4$ as a function of sample size. Effect of the addition of traces of $TiCl_4$ to the carrier gas. Temperature of analysis: 75°C.

As Fig. 12 shows, tailing of the $TiCl_4$ peak is reduced markedly by the addition of about 100 ppm v/v of $TiCl_4$ (a concentration of the order of the detection limit). Even more marked is the improvement of the quantitative result: the elimination of the effects of sample size and injection sequence and the complete recovery (see also Fig. 16 and Table 7).

Recovery of $VOCl_3$. Since $VOCl_3$ was not available in sufficient quantity for the preparation of test mixtures, we used a different technique. Small amounts of vanadium and V_2O_5 were converted into $VOCl_3$ by chlorination on a microscale in situ. (Chlorina-

TABLE 7

Recovery of Titanium Tetrachloride and Gallium Trichloride as a Function of the Sequence of Injection
Effect of the Addition of Traces of Component to the Carrier Gas
(Sample size: approx. 2 μl of component)

Component	Temp. of analysis, °C	Addition to carrier gas	Result of analysis, % of theory				
			1st injection	2nd injection	3rd injection	4th injection	5th injection
$TiCl_4$	75	None	64.5	77.9	76.0	80.2	81.7
$TiCl_4$	75	~10 ppm v/v $TiCl_4$	85.3	80.0	85.6	89.3	
$TiCl_4$	75	~100 ppm v/v $TiCl_4$	99.4	99.4	99.6	99.4	99.2
Ga_2Cl_6	150	None	61.9	90.7	87.2	94.2	
Ga_2Cl_6	150	~100 ppm v/v Ga_2Cl_6	84.1	76.7	92.2	102.4	95.5
Ga_2Cl_6	150	~700 ppm v/v Ga_2Cl_6	99.2	98.0	97.8	99.5	101.8

tion of the metal was carried out at 700°C in the presence of oxygen, while the reaction of the oxide with chlorine took place at 900°C.) The amounts of vanadium and V_2O_5 were determined by weighing on a microbalance to 0.01 mg.

As can be seen in Fig. 17, there is a proportional relationship between sample size and peak size, which means that recovery is at least constant. Moreover, consistent results are obtained from different series of measurements, using either the metal or the oxide as starting material.

To check the recovery, samples of tin[*] were chlorinated in the same way. Assuming complete conversion of this metal and no losses of $SnCl_4$ in the column (which has been proved before), the average over-all recovery of $VOCl_3$ based on impure metal or oxide was found to be 93%. Since this includes possible deviations from stoichiometry of the conversion step and the purity of the starting materials (about 95%), it can be concluded that the recovery of $VOCl_3$ from the column is satisfactory. Losses in the column, if any, are limited to a few per cent.

[*] Actually a homogeneous tin/lead alloy containing 10.2 wt % Sn was chlorinated rather than pure tin in order to reduce the weighing error.

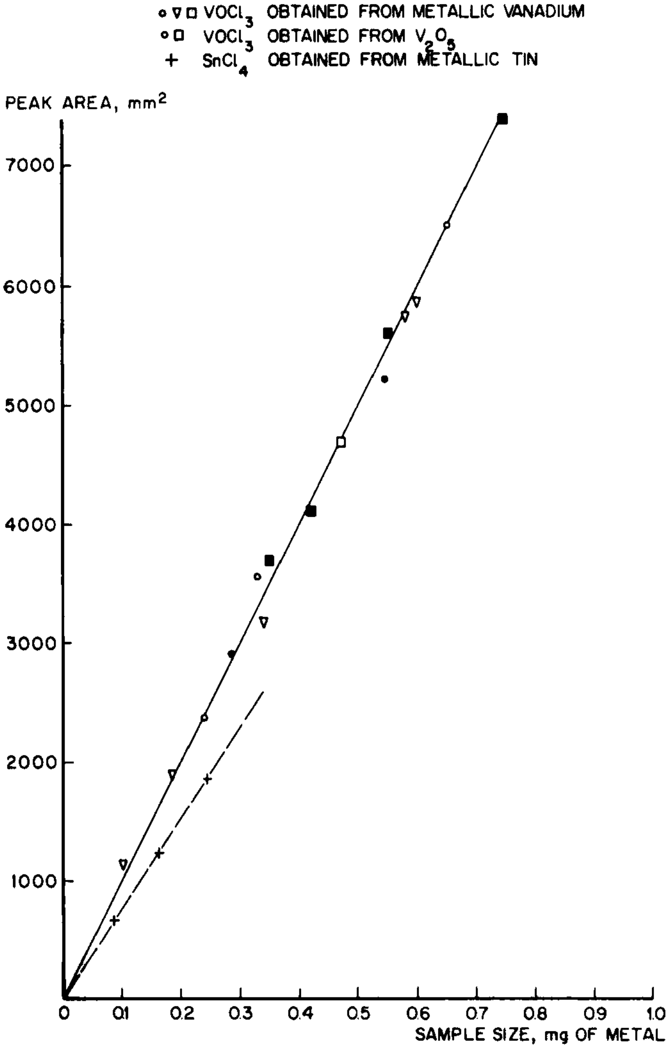


FIG. 17. Relationship between sample size and peak area for $VOCl_3$ and $SnCl_4$ (points differently marked belong to different series of measurements).

Quantitative Analysis of Mixtures. Some results of quantitative gas-chromatographic analysis of liquid mixtures of known composition are presented in Table 8. It is seen from this table that the gas-chromatographic figures (calculated by means of theoretical response factors) are in good accordance with the composition determined by weighing. The accuracy obtained is of the

TABLE 8

Examples of Quantitative Analyses of Mixtures of Inorganic Chlorides (Results calculated with theoretical response factors)

Mixture No.	Temp. of analysis, °C	Components	Content, wt %								Deviation from theory, wt %
			Experimental						Mean found	Theoretical	
1	75	$SiCl_4$	18.5	18.5	17.8	18.1	17.7		18.1	18.6	−0.5
		$GeCl_4$	20.2	20.2	20.2	20.0	20.7		20.2	20.2	0.0
		$SnCl_4$	61.3	61.5	62.0	61.9	61.6		61.7	61.2	0.5
2 + 3 (duplicate mixtures)	75	$SiCl_4$	32.4	32.0	31.8	32.5			32.2	32.6	−0.4
		$GeCl_4$	25.2	25.7	25.5	26.2			25.6	25.3	0.3
		$SnCl_4$	42.4	42.3	42.7	41.3			42.2	42.1	0.1
4	75	$SiCl_4$	21.1	21.6	21.9	21.3			21.5	21.8	−0.3
		$SnCl_4$	78.9	78.4	78.1	78.7			78.5	78.2	0.3
6	75	$SiCl_4$	38.0	38.0	38.4				38.1	38.3	−0.2
		$SnCl_4$	62.0	62.0	61.6				61.9	61.7	0.2
5	75	$SiCl_4$	14.7	14.6	14.5	14.6	14.5	14.3	14.5	14.8	−0.3
		$GeCl_4$	33.6	32.8	33.3	33.3	33.3	33.1	33.2	32.1	1.1
		$AsCl_3$	51.7	52.6	52.2	52.1	52.2	52.6	52.3	53.1	−0.8
20	125	$AsCl_3$	28.0	28.0	27.6				27.9	28.1	−0.2
		$SbCl_3$	72.0	72.0	72.4				72.1	71.9	0.2
15	75	PCl_3	24.1	24.1	23.6	24.9	25.2	24.9	24.4	24.7	−0.3
		$POCl_3$	75.9	75.9	76.4	75.2	74.8	75.1	75.6	75.3	0.3
13	75	CCl_4	29.0	28.7	28.4				28.7	27.3	1.4
		$POCl_3$	71.0	71.3	71.6				71.3	72.7	−1.4
14	75	PCl_3	29.6	29.8	30.0	30.0	30.0		29.9	30.0	−0.1
		$C_2H_3Cl_3$	70.4	70.2	70.0	70.0	70.0		70.1	70.0	0.1
16	75	SO_2Cl_2	25.6	25.5	25.0	25.4			25.4	25.6	−0.2
		S_2Cl_2	74.4	74.5	75.0	74.6			74.6	74.4	0.2
8	75	SCl_2	19.5	19.3	19.4				19.4	19.1	0.3
		$SOCl_2$	21.3	21.9	22.0				21.7	22.3	−0.6
		S_2Cl_2	59.2	58.8	58.6				58.9	58.6	0.3
10, 12 (duplicate mixtures)	75	CCl_4	27.5	26.9	26.4	26.0	26.0		26.6	25.6	1.0
		CrO_2Cl_2	72.5	73.1	73.6	74.0	74.0		73.4	74.4	−1.0
19[a]	75	$SiCl_4$	12.7	12.8	13.3	12.8	12.6	12.7	12.8	12.4	0.4
		$SnCl_4$	38.2	38.2	38.3	38.0	38.3	38.3	38.2	38.2	0.0
		$TiCl_4$	49.1	49.1	48.4	49.2	49.1	49.0	49.0	49.4	−0.4
22[b]	150	$AsCl_3$	47.3	48.0	48.0	47.2	45.8		47.3	46.8	0.6
		Ga_2Cl_6	52.7	52.0	52.0	52.8	54.2		52.7	53.2	−0.6

[a] Analyses carried out with addition of traces of $TiCl_4$ to carrier gas.

[b] Analyses carried out with addition of traces of Ga_2Cl_6 to carrier gas.

same order as can be attained in normal gas-chromatographic analysis of unreactive organic substances.

The results for sulfur dichloride merit further discussion. The composition of mixture 8 of Table 8 (containing SCl_2, $SOCl_2$, and S_2Cl_2) was calculated taking into account the amount of

S_2Cl_2 already present in the SCl_2 sample. The close agreement between calculated and experimentally found figures shows that no additional formation of S_2Cl_2 occurs to any significant extent within the column. This is noteworthy, since SCl_2 is known to dissociate at higher temperatures. Evidently dissociation rate and/or equilibrium at the temperature of operation (75°C) are sufficiently favorable to permit quantitative gas-chromatographic analysis. This conclusion should apply even more forcibly to an analysis at room temperature (see the note on page 51 pertaining to the determination of the purity of SCl_2).

TABLE 9

Repeatability of the Gas Chromatographic Determination of Silicon Tetrachloride and Tin Tetrachloride
(Determinations carried out on different days)

Temperature of analysis:	75°C		100°C		125°C	
Number of determinations:	9		9		9	
Component:	$SiCl_4$	$SnCl_4$	$SiCl_4$	$SnCl_4$	$SiCl_4$	$SnCl_4$
Theoretical content, wt %:	22.6	77.4	22.6	77.4	22.6	77.4
Mean result, wt %:	22.5	77.5	23.6	76.4	23.9	76.1
Maximum result, wt %:	22.9	77.9	24.0	76.6	24.7	77.3
Minimum result, wt %:	22.1	77.1	23.4	76.0	22.7	75.3
Standard deviation, wt %:	0.2^3	0.2^3	0.1^9	0.1^9	0.6^5	0.6^5
Relative standard deviation, %:	1.0	0.3^0	0.8^4	0.2^5	$2.^9$	0.8^4

Table 9 gives the results of three series of analyses, carried out on a mixture of $SiCl_4$ and $SnCl_4$ to obtain figures on the repeatability of the gas-chromatographic procedure. For the series carried out at 75 and 100°C (with samples of about 5-μl size), nearly the same standard deviation was found, 0.2 wt %. The series carried out at 125°C show a somewhat lower precision (standard deviation 0.6 wt %), possibly as a result of the reduced peak areas. (Since the peaks were narrower, the sample size was reduced to about 2 μl to keep the signal well within the linear range of the detector.)

CONCLUSIONS

Except for the unstable tetrachloride of vanadium and pentachloride of antimony, all inorganic chlorides examined have been found sufficiently stable to permit a gas-chromatographic separation. With proper choice of column materials, and some adaptation of apparatus and injection technique to the reactivity of these compounds, quantitative analyses are possible with an accuracy equal to that normally obtained in GLC.

At the normal operating temperatures (125°C or below) Kel-F 40 columns are quite stable and may be used for months. The gas density detector has been in operation for at least a year and has given trouble-free service during that period.

The favorable evidence which the present study affords regarding the gas-chromatographic analysis of metal chlorides boiling up to about 250°C, promises well for a direct and rapid analysis of metals and alloys. When heat-stable stationary phases of sufficient inertness can be found for the analysis of the higher-boiling inorganic chlorides, too, the range of elements covered may become very wide.

An investigation into the possibilities of converting metals and alloys into the chlorine derivatives of their constituent elements, as well as examples of metal analysis by gas chromatography, will be described in a subsequent paper.

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