

GAS-LIQUID CHROMATOGRAPHY OF VOLATILE METAL HALIDES

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In general, gas chromatography has largely been concerned with the separation of volatile organic compounds and very little has been done with metals. Development of high temperature techniques has now opened up this area. Two trends are apparent in the results reported so far. One involves the use of fused salts as the immobile phase while the other is the use of slightly volatile liquids such as silicones or vacuum greases usually encountered in high temperature work. Both have advantages and disadvantages. The former, while useful at very high temperatures, are difficult to prepare on the support, especially in anhydrous form, and are subject to reaction with the solutes. The latter are lost from the column, redistribute on the support, may be thermally unstable, and are capable of reaction with the solutes.

DE BOER¹ chromatographed a zinc-cadmium alloy on lithium chloride at 620°. There was evidence that separation was not due to simple distillation but involved interaction between the solute and the immobile phase. JUVET AND WACHI² used a eutectic mixture of BiCl₃-PbCl₂ at 240° in a separation of titanium(IV) chloride and antimony(III) chloride to avoid volatile organic partitioners and undesirable reactions between solute and immobile phase. With regard to fused salts, it is interesting to note that HANNEMAN, SPENCER AND JOHNSON³ chromatographed C₁₅ to C₂₈ *n*-paraffins and polyphenyls on a eutectic of alkali metal nitrates at 300°. On the basis of the variation of HETP with flowrate, the linear relation between the log retention time and carbon number for homologous series, and symmetrical peaks, they concluded that molten salt phases behave in the same manner as organic liquids. Apparently small samples were necessary to obtain these results. The results indicate only linear kinetics and not necessarily solution in the immobile phase. Consideration of adsorption of the solute at the liquid-gas or liquid-liquid interface has been neglected in all accounts of chromatographic theory^{4,5} and this phenomenon may prove to be of major importance with fused salts. The short retention times reported by HANNEMAN *et al.* may be an indication of this since such an adsorption might not involve appreciable diffusion into and out of the immobile phase thus reducing the period of fixation by this phase.

DUSWALT⁶ suggested that since the acetyl acetonates of Mn, Pb, Zn, Co, Ni, Fe, Cu, Be, Hg, Al, In, U, Th, and Cr are thermally stable, they ought to be considered as solutes for gas chromatographic (GC) separation since a number of them are known to be volatile. He prepared and tested the acetyl acetonates of Al, Be, Cd, Hg, Sc,

and Zn obtaining peaks for Be, Sc, and Zn on silicone oil and propylene glycol-adipic acid polymer supported by Celite at 225°. Failure to obtain peaks for Al and Hg was attributed to too low a temperature of the sample injection unit. Very broad peaks were traced to this same source. We feel this same deficiency in the work reported here.

FREISER⁷ separated tin(IV) chloride from titanium(IV) chloride at 102° using *n*-hexadecane (31% by weight) on Chromosorb as the immobile phase. The ratio of the vapor pressures of tin(IV) chloride to titanium(IV) chloride (1.91) was nearly the inverse of the ratio of retention times (2.32). The peaks were very nearly symmetrical and well resolved. A small minor peak, very close to the air peak, was observed with the sample containing titanium(IV) chloride (see Fig. 4A for this same result in the present work). Whenever a large quantity of either of these solutes was used, the peak was preceded by a "foot" never exceeding 1 mV on a 10 mV range (see Fig. 4B); the recorder went off scale with the major peak in these cases. The foot or shoulder is very similar in appearance and formed under the same circumstances as those observed by WEURMAN AND DHONT⁸ in the chromatography of alcohols on polyethylene glycol. They suggested that the immobile phase decomposed to give formic acid which then esterified with the alcohol to give the faster moving ester. KIESER AND SISSONS⁹ attributed the effect to reaction with formaldehyde and formic acid present as impurities in the polyethylene glycol used to prepare the partitioner. It would seem that in either case the ester would continually be produced in the region of the column containing the migrating alcohol and appear as a shoulder rather than as a well defined peak as it is eluted from the alcohol zone. In our case, a decomposition product might be produced in the zone containing the inorganic halide and the product then moving out of this region to give a shoulder. This phenomenon might well be discussed from the viewpoint of KELLER AND GIDDINGS¹⁰ as a special case of multiple-zone formation. We have also observed the aforementioned peak superimposed on these shoulders resulting in some rather unusual concentration profiles indeed. These secondary effects were always minor compared to the major peaks and there was no confusion in identifying the major constituent. Recognizing that the column was being operated appreciably above the recommended maximum temperature of 40° for the *n*-hexadecane¹¹, little more was done with this partitioner, it having been established that separations were feasible. In spite of this higher temperature, there was no drift in the base line or condensation of partitioner in the outlet tube which are generally the symptoms of loss of immobile phase. An extension of this investigation has already been reported¹².

WACHI¹³ attempted the chromatography of tin(IV) chloride and titanium(IV) chloride on silicone grease and Apiezon M grease supported on firebrick in stainless steel columns with the sample port at 150° and the column at 125°. Failure to obtain peaks was attributed to complete reaction of the chlorides with the greases and the walls of the column. Chromatograms of iron(III) chloride on these two partitioners at 325° also failed. WACHI then turned to fused inorganic eutectics in seven foot glass columns (the fused salt partitioners reacted with stainless steel) and reported:

(1) A chromatogram of tin(IV) chloride on a 41 % by weight cadmium chloride-potassium chloride eutectic (m.p. 383°) at 464° (sample injector at 210°). (2) Partial resolution of tin(IV) chloride and antimony(III) chloride on this eutectic at 474°. Base line drift was attributed to temperature variation of the furnace. (3) Chromatograms of tin(IV) chloride and titanium(IV) chloride on 37 % by weight aluminum chloride-sodium chloride at 145° and 143° respectively (sample injector at 109°). (4) Partial resolution of a mixture of tin(IV) chloride and titanium(IV) chloride on this eutectic at 145°. Poor results were attributed to the insolubility of the latter compound in the eutectic. (5) Failure of nitrate eutectics to separate the transition metal chlorides due to the oxidizing properties of the nitrates. (6) GSC chromatograms of tin(IV) chloride and mixtures of it with titanium(IV) chloride on a 12 ft. column of C-22 firebrick at 141°. Resolution was very poor and the retention time was short. In all these cases flowrates were either 20 or 30 ml of nitrogen per min and retention times were all very nearly 5 min which is considerably less than we have observed. WACHI concludes that the eutectics act as a partition medium. We do not substantiate his conclusion that metal columns cannot be used with volatile inorganic materials because of reaction with the metal. We do not contest the statement that the eutectics react with the metal. The preparation of coiled glass columns, packing them, and coating of the firebrick with an anhydrous eutectic salt present some considerable challenges in technique. WACHI's use of a flash vaporizer as the sample injection unit is an improvement on DUSWALT's and our own apparatus.

We estimate the vapor pressures of titanium(IV) chloride and antimony(III) chloride to be 6530 mm and 1197 mm respectively at 240°¹⁴. The ratio of the vapor pressures of the first to the second is 5.46 while the inverse ratio of retention times is 6.0 for the fused salt immobile phase (JUVET AND WACHI²). Here, as with the *n*-hexadecane, emergence is ordered according to vapor pressure and little or no chemical interaction or, at least, the same degree of interaction of solute and immobile phase is indicated.

TABLE I
VOLATILITY OF CERTAIN METAL HALIDES

Metal	Boiling point (°C)			Metal	Boiling point (°C)		
	Cl	Br	I		Cl	Br	I
Boron(III)	12.5	90.1 ^a	210	Antimony(III)	223	280	401
Silicon(IV)	57.6	153	290	Niobium(V)	240.5	270	—
Germanium(IV)	83.1	186.5	—	Tantalum(V)	242	320	—
Tin(IV)	114.1	202 ^b	341	Gold(III)	265 ^s	—	—
Arsenic(III)	130.2	221	403	Molybdenum(V)	268	—	—
Titanium(IV)	136.4	230	> 360	Tungsten(V)	275.6	333	—
Vanadium(IV)	149.5 ^c	—	—	Mercury(II)	302	322	354
Antimony(V)	140	—	400.6	Iron(III)	315	—	—
Aluminum(III)	177.8 ^s	263.3 ^d	382	Zirconium(IV)	300 ^s	—	—
Gallium(III)	201.2	278.8	345 ^s	Tungsten(VI)	346.7	—	—

^a 740 mm Hg pressure

^b 734 mm Hg pressure

^c 755 mm Hg pressure

^d 747 mm Hg pressure

^s Sublimes

That inorganic halides are likely solutes for GC separation is demonstrated by Table I¹⁴.

The investigation described here involves tin(IV) chloride, titanium(IV) chloride niobium(V) chloride, and tantalum(V) chloride on several partitioners at different temperatures.

APPARATUS

Analyzer

Analyses were made with a Cenco No. 70130 Vapor Phase Analyzer (Central Scientific Co., Chicago, Ill.) equipped with a katharometer detector. Column, katharometer, and sample injection unit were all at the same temperature. Concentration profiles were recorded on a Leeds and Northrup Speedomax Model S, variable range, variable sensitivity recorder of 1 sec response time and 30 in./h chart speed. A dry box containing a drying agent and through which dry nitrogen was passed, was placed above the sample port to permit sample introduction under anhydrous conditions. Fuming was still observed, however. This same dry box was used in the preparation of solutions. Sample introduction was by a 0.25 ml hypodermic syringe. Driving pressure was measured by a mercury manometer placed at the source of the helium carrier and flowrates were measured by means of a soap-film flowmeter¹¹ and stopwatch.

Columns

The columns were all of coiled 0.25-in. copper tubing, 1.60 m in length (actual length of packing).

Partitioning agent

The partitioning agents were supported by Red Chromosorb (Johns-Manville, New York, N.Y.) dried at 125° for 48 h before application of the immobile phase. The immobile liquid was applied by dissolving it in diethyl ether and then evaporating off the solvent while in contact with the support with constant stirring. The material was then kept in a vacuum desiccator at reduced pressure for two days to insure removal of the ether and size graded to 30–60 mesh. Quantities of the packing were weighed, the column packed, and the remaining packing weighed to determine the actual weight of material in the column. Weighed samples of the materials were also extracted with diethyl ether using a Soxhlet extractor to determine the quantity of immobile phase present. Table II summarizes the important characteristics of each column. Squalane column I was used in the chromatography of the individual solutes at the three different temperatures while column II was used in the chromatography of a mixture of the four at 200°. The columns were conditioned by passing helium through them for 4–5 h at 100° before analyses were made.

Solutes

Tin(IV) chloride (J. T. Baker Chemical Co., Phillipsburg, N.J., C.P.) and titanium(IV) chloride (Kahlbaum, Chemische Fabrik, Adlershof bei Berlin) were used as the liquids (sample sizes of 0.015 to 0.02 ml). Niobium(V) chloride (Stauffer Chemical

Co., New York, N.Y.) and tantalum(V) chloride (Stauffer Chemical Co.), solids at room temperature, were dissolved in redistilled carbon tetrachloride and saturated solutions used in the chromatography of the individuals. These liquids and solutions were stored in glass-stoppered flasks in a desiccator while not in use.

TABLE II
COLUMN CHARACTERISTICS

<i>Immobile phase</i>	<i>Per cent by wt.</i>	<i>Total weight of immobile liquid phase in the columns (g)</i>	<i>Column density (g/m)</i>
<i>n</i> -Octadecane ^a	33.9	6.41	11.81
Squalane ^b			
Column I	34.4	6.67	12.12
Column II	34.4	6.68	12.13
Apiezon Tc	28.6	3.74	8.18 ^f
Silicone oil ^d	36.0	6.82	11.84
Paraffin ^e	38.1	4.09	6.71 ^f

^a Eastman Organic Chemicals, D.P.I. (Practical), Rochester, N.Y.

^b Eastman Organic Chemicals, D.P.I. (White Label), Rochester, N.Y.

^c Apiezon Products Limited, James G. Biddle Co., Philadelphia, Pa.

^d Silicone Oil 81705, General Electric, Waterford, N.Y.

^e "Fruitmaster" Paraffin Wax, Penola Oil Co., Bayonne, N.J.

^f The immobile phases did not "flow" well because of the cohesive properties of the liquid and they gave a less dense packing.

The obvious objection to the procedure for the solutions is that the sample volume is quite large (about 0.15 to 0.20 ml) so that migration is not initiated from a narrow zone. Fortunately the solute and solvent peaks are widely separated. The recorder was set at 20 mV until the solvent peak had passed and then changed to 5 mV to pick up the smaller solute peaks. Secondly, the temperature of the sample injection unit does not insure immediate vaporization of the solute. Niobium(V) chloride melts at 194° while tantalum(V) chloride melts at 221°¹⁴ which means the sample port temperature is in the region of the melting point. Obviously the material does not enter the column as a "plug" and excessive peak broadening is to be expected. A high temperature sample injector is needed.

Finally, niobium(V) chloride and tantalum(V) chloride were added to a 50-50 (by volume) mixture of tin(IV) chloride and titanium(IV) chloride to give a saturated solution. This mixture was chromatographed on squalane (column II) at 200°. The sample volume was such that the amounts of tin and titanium chlorides would be the same as those used in the chromatography of the pure solutes. In spite of this adjustment, the recorder response was much less with the mixture. This, coupled with the appearance of a precipitate on making up the solution, indicated interaction of these solutes in an as yet undetermined manner. Fig. 3 is the concentration profile of this chromatogram.

RESULTS

Flowrates were measured with a stopwatch every 10 min for short duration chromatograms and every 30 min for longer⁶ chromatograms. Average flowrates were used when the individual values showed a random variation about the mean. If, however, there was a trend in the flowrate due to a drop in the driving pressure, a least squares line was fitted to a plot of flowrate *vs.* time, and the retention volume determined from the empirical equation for the variation of flowrate with time. Where this was done, the average driving pressure was used in correcting for the pressure drop across the column. Uncertainties in the retention volumes are based on average deviations from the mean or average deviation from the least squares line. Temperature variations of the column are maximum.

Measurements, terminology, and symbols are those recommended by AMBROSE, KEULEMANS AND PURNELL¹⁵ and JOHNSON AND STROSS¹⁶. V_g is the retention volume of the solute per gram of immobile phase, relative to the air peak, measured in terms of dry carrier gas at standard conditions. Table III gives the values of $\log V_g$ at various

TABLE III
LOG SPECIFIC RETENTION VOLUMES

	$\log V_g$	$1/T \times 10^4$		$\log V_g$	$1/T \times 10^4$	
<i>Squalane column I</i>			<i>n-Octadecane</i>			
Sn	2.127	26.80	Sn	2.169	26.80	
	1.534	23.64			1.531	23.63
	1.099	21.12				
Ti	2.177	26.77	Ti	2.549	26.77	
	1.651	23.64	<i>Silicone</i>			
	1.255	21.12	Sn	1.777	26.77	
Nb	2.909	23.61			1.786	26.77
	2.534	21.14			1.169	23.66
Ta	2.922	21.14		0.702	21.15	
			<i>Paraffin</i>			
<i>Squalane column II</i>			Sn	2.075	26.71	
Sn	0.775	21.13			1.512	23.62
					1.029	21.13
Ti	1.127	21.13	Ti	2.508	26.78	
Nb	2.513	21.13			2.473	26.70
					1.915	23.65
Ta	2.732	21.13			1.496	21.13

temperatures and partitioners. Fig. 1 is a plot of $\log V_g$ *vs.* the reciprocal of the absolute temperature for all the solutes on squalane. Fig. 2 is a similar plot for tin(IV) chloride and titanium(IV) chloride only on different partitioners at different temperatures. In Table IV we report column inlet and outlet pressures and flowrates of dry gas at the column temperature and outlet pressure since the actual operating condi-

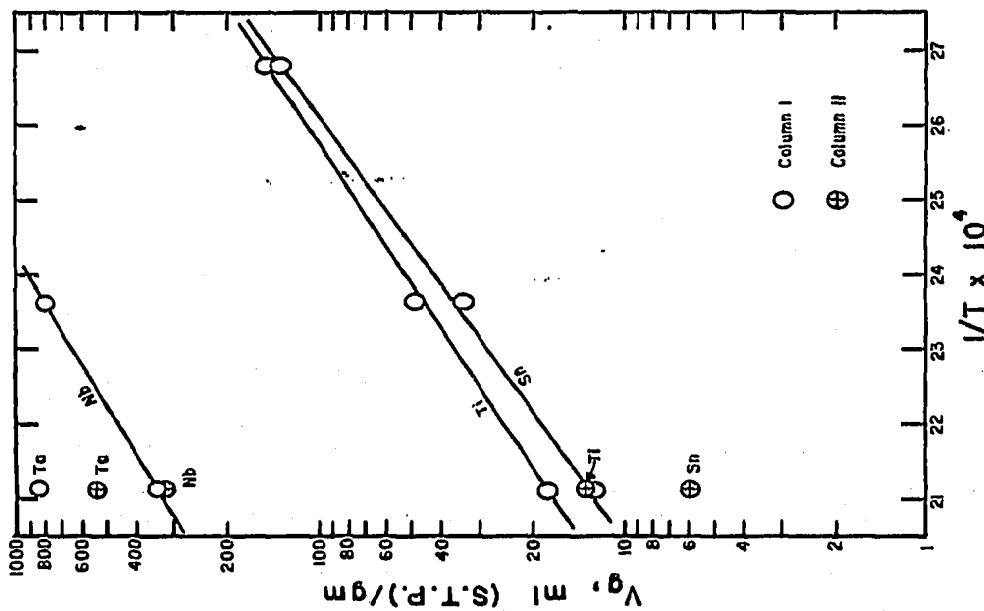


Fig. 1. Log of the retention volume (ml of dry helium at 1 atm. and 0° corrected for the pressure drop) per g of partitioning liquid vs. the reciprocal temperature for tin(IV) chloride, titanium(IV) chloride, niobium(V) chloride, and tantalum(V) chloride on two different columns of squalane supported by firebrick.

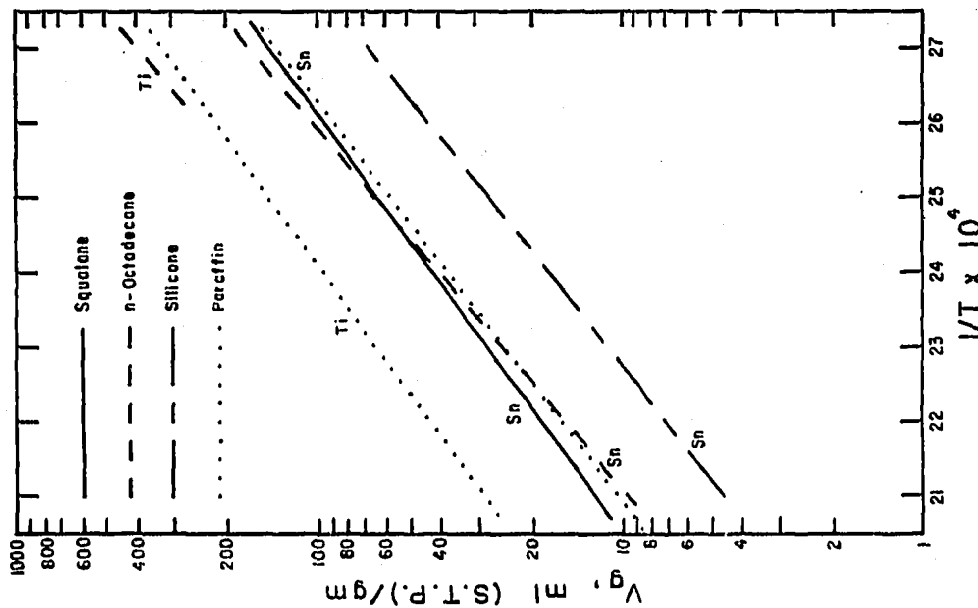


Fig. 2. Log of the retention volume (ml of dry helium at 1 atm. and 0° corrected for the pressure drop) per g of partitioning liquid vs. the reciprocal temperature for tin(IV) chloride and titanium(IV) chloride on columns of *n*-octadecane, squalane, paraffin wax, and silicone oil supported by firebrick.

TABLE IV
 OPERATING CONDITIONS

	Temperature ^a (°C)	Inlet pressure (cm Hg)	Outlet pressure (cm Hg)	Flowrate ^b (ml/min)	V_g (ml(STP)/g)
<i>Squalane column I</i>					
Sn	99.8 ± 0.6	81.2	69.7	36.5 ± 0.4	134 ± 2
	149.7 ± 0.5	84.1	69.6	40.0 ± 0.4	34.2 ± 0.3
	200.1 ± 0.3	91.8	69.6	60.3 ± 0.5	12.56 ± 0.09
Ti	100.3 ± 0.9	83.3	69.8	41.6 ± 0.2	150.2 ± 0.6
	149.7 ± 0.7	84.0	69.6	39.9 ± 0.2	44.8 ± 0.1
	200.2 ± 0.4	91.7	69.6	58.9 ± 0.3	18.0 ± 0.1
Nb	150.3 ± 0.5	88.4	69.6	52.8 ± 0.4	812 ± 9
	199.7 ± 0.5	92.1	69.7	58.0 ± 0.7	342 ± 4
Ta	199.8 ± 0.8	94.9	70.2	65.2 ± 0.4	836 ± 6
<i>Squalane column II</i>					
Sn	199.9 ± 0.5	85.1	70.1	40.2 ± 0.2	5.96 ± 0.03
Ti	199.9 ± 0.5	85.1	70.1	40.2 ± 0.2	13.4 ± 0.1
Nb	199.9 ± 0.5	85.1	70.1	40.2 ± 0.2	326 ± 2
Ta	199.9 ± 0.5	85.1	70.1	40.2 ± 0.2	539 ± 3
<i>n-Octadecane</i>					
Sn	99.9 ± 0.5	97.8	70.1	38.7 ± 0.2	147.6 ± 0.6
	149.9 ± 0.3	105.2	70.3	42.2 ± 0.5	34.0 ± 0.3
Ti	100.3 ± 0.7	97.7	70.2	36.9 ± 0.2	354 ± 3
<i>Silicone</i>					
Sn	100.3 ± 0.3	78.0	70.2	28.6 ± 0.2	59.8 ± 0.6
	100.3 ± 0.7	81.9	70.4	44.6 ± 0.6	61.1 ± 0.9
	149.4 ± 0.4	80.2	70.2	35.2 ± 0.2	14.76 ± 0.07
	199.6 ± 0.4	81.7	70.1	37.1 ± 0.6	5.04 ± 0.09
<i>Paraffin</i>					
Sn	101.1 ± 0.3	70.6	69.9	51.3 ± 0.1	118.8 ± 0.2
	150.0 ± 0.8	70.5	69.7	57.0 ± 0.8	32.5 ± 0.5
	200.0 ± 0.2	70.9	69.8	72.8 ± 0.7	10.7 ± 0.1
Ti	100.2 ± 0.6	70.5	69.9	51.1 ± 0.3	322 ± 2
	101.2 ± 0.6	70.6	69.8	68.1 ± 0.6	297 ± 3
	149.6 ± 0.4	70.5	69.7	57.8 ± 0.3	82.3 ± 0.2
	200.0 ± 0.2	70.9	69.8	72.3 ± 0.6	31.3 ± 0.2

^a Deviations are the maximum observed.

^b Flowrates are for the dry gas at the outlet pressure and temperature of the column and are not corrected for the pressure drop. Deviations are the average deviations from the mean or the least squares plot.

tions dictate column performance. Table V gives the values of the constants of the equation

$$\log V_g = a + \frac{b}{T} \times 10^4$$

TABLE V
CONSTANTS OF THE LEAST SQUARES PLOT FOR

$$\log V_g = a + \frac{b}{T} \times 10^4$$

Immobile phase	Solute	a	b
Squalane (column I)	SnCl ₄	-2.60	0.176
	TiCl ₄	-2.18	0.161
	NbCl ₅	-0.814	0.158
n-Octadecane	SnCl ₄	-3.22	0.201
Silicone	SnCl ₄	-3.29	0.189
Paraffin wax	SnCl ₄	-2.92	0.187
	TiCl ₄	-2.29	0.178

as determined by the fit of a least squares line to the data of Table III.

Two attempts were made to chromatograph tin(IV) chloride on Apiezon grease at 100° with no success, which agrees with WACH's results¹³. This solute did chromatograph on the silicone oil but titanium(IV) chloride did not appear either at 100° or 150°. We assume the latter reacted with the partitioning agent. Two results are reported at 100° ($V_g = 59.8 \pm 0.6$ and 61.1 ± 0.9) which are within experimental error of one another and differ by 2%.

Fig. 1. shows only fair reproducibility between squalane columns I and II. Figs. 3 and 4 are excellent demonstrations of difficulties to be encountered in this work. Fig. 4A is the concentration profile of tin (IV) chloride on paraffin at 100°. The first peak, attributed to some artifact in the original sample, probably hydrogen chloride formed in the solution on standing, is well defined and typical of the results expected in

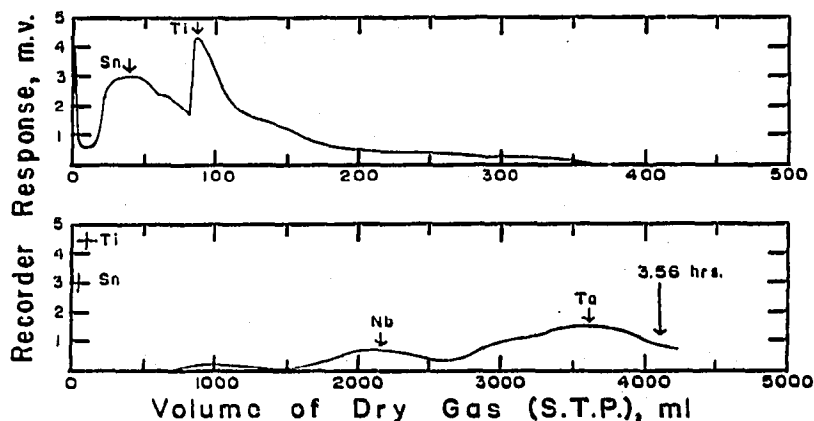


Fig. 3. Concentration profile of a chromatogram of a mixture of tin(IV) chloride, titanium(IV) chloride, niobium(V) chloride, and tantalum(V) chloride on squalane at 200° and helium flowrate of 40.2 ml/min. The volume scale and flowrate is for ml of dry gas at 1 atm. and 0° corrected for the pressure drop.

good chromatography. Fig. 4B shows the concentration profiles of titanium(IV) chloride on this same column. Each peak is preceded by the aforementioned shoulder, and, as can be seen from the peak positions, this shoulder would interfere with the peak for tin(IV) chloride. This may explain the poor resolution of tin(IV) chloride

and titanium(IV) chloride shown in Fig. 3. The shoulder is more predominant and the major peak smaller at the slower flowrate than at the faster. We ascribe this to an increased opportunity for reaction between solute and immobile phase at the slower flowrate. Since the sample sizes are probably different for the two runs, the

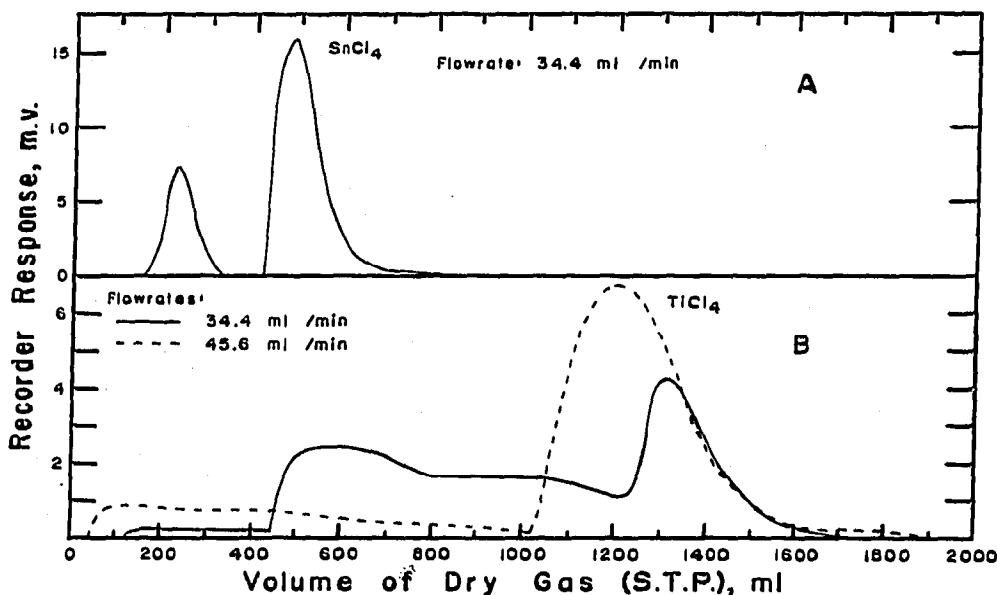


Fig. 4. Concentration profile of tin(IV) chloride and titanium(IV) chloride on paraffin wax at 100° and different flowrates of helium. The volume scale and flowrate is for ml of dry gas at 1 atm. and 0° corrected for the pressure drop. A. Tin(IV) chloride at 34.4 ml/min. B. Titanium(IV) chloride at 34.4 and 45.6 ml/min.

ratio of the areas under the shoulder to that under the entire curve was taken as a measure of the extent of the reaction. At the lower flowrate this ratio is 0.64 while at the faster it is 0.22.

CONCLUSIONS

It is apparent from Fig. 2 that hydrocarbon phases are satisfactory in the separation of the metal halides. In so far as tin(IV) chloride is concerned, the three paraffins used behave in very much the same manner. Apiezon grease and silicone oil react with the solutes. The normal alkanes appear more satisfactory than branched chain compounds. If paraffin wax is assumed to be more branched than squalane, the latter having six methyl branches per molecule, then one may explain the increased predominance of the shoulder with increased branching by assuming the solutes to act on the tertiary hydrogen of the partitioning liquids to remove a hydrogen atom or, as a Lewis acid, to remove a hydride ion. The remaining free radical or carbonium ion could rearrange in a number of ways. The union of the solute and the hydrogen might then decompose to release hydrogen chloride and a reduced form of the solute. As mentioned earlier, this artifact could interfere with preceding solute peaks (Fig. 4). Asymmetry of the solute peaks seems to increase as one goes to higher molecular weight alkanes or with branching. We conclude that normal alkanes are the most

satisfactory liquids, but, unfortunately, they are generally unsuitable at high temperature because of their volatility.

It is obvious from Fig. 3 that this separation is ripe for attack by temperature-programmed techniques. Tin(IV) chloride and titanium(IV) chloride appear in the first 100 ml of carrier while the chromatogram is not completed until about 4 l of carrier.

The greatest difficulty in this work, especially if quantitative results are desired, is the preparation and introduction of measured samples under anhydrous conditions. We are presently engaged in filling glass ampoules with weighed quantities of solute and using a "crusher" type injection system. Obviously a prevaporization sample chamber is also required.

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SUMMARY

The literature on the gas chromatography of volatile metal compounds is reviewed.

Results are reported for the gas-liquid chromatography of tin(IV) chloride, titanium(IV) chloride, niobium(V) chloride, and tantalum(V) chloride on *n*-octadecane, squalane, silicone oil, paraffin wax, and Apiezon grease at 100°, 150°, and 200°. Results indicate normal alkanes to be the best partitioners and that branched alkanes lead to reaction on the column. Suggestions are made concerning anhydrous conditions in handling samples, sample prevaporization, and the use of temperature programming.

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