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## SUPERHIGH TEMPERATURE GAS CHROMATOGRAPHY

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## SUMMARY

At red heat temperatures and higher, the conditions of gas chromatographic separation change essentially, since the separated components, packing and even the column and detector walls are in a state of higher chemical activity.

When designing an apparatus for superhigh temperature gas chromatography, the detector problem is the most difficult. Many kinds of detectors used at present are unsuitable under these conditions and considerable modifications of others are necessary. Pneumatic detectors are the most useful for superhigh temperature detection.

At temperatures between 500 and 1000° the separation is often complicated by chemical reactions which can take place in the column. For instance, irreversible absorption of metallic K and Na, and  $\text{PbCl}_2$  and  $\text{SnCl}_2$  with many materials, destruction of  $\text{CdI}_2$ , reaction between S and Se on introduction of such a mixture into the column have been observed. However, the successful separation of some metals and halides and good results for the direct quantitative analysis of Zn-Cd binary alloys allows us to hope that further investigation in this field will give interesting results.

## INTRODUCTION

Up to the present gas chromatography has been used at temperatures not greater than 450–500°. Only one attempt has been made to separate metal (Zn and Cd) vapours at 620° (ref. 1). The results were promising, but due to the nonavailability of a detector, the author did not obtain a chromatogram.

It may be assumed that a gas chromatographic separation can be realised at any temperature when there is a solid phase with a large surface area (adsorbent or solid support) a liquid phase with a small vapour pressure (in the case of gas-liquid chromatography), an inert carrier gas and a volatile substance whose vapours can be retained by the adsorbent or resolved in the liquid phase. These conditions seem to be realisable at temperatures up to 3000° and even somewhat higher. Superhigh temperature gas chromatography differs considerably from the ordinary case, as the packing and separating components, as well as the column and detector walls at separation temperature are in a state of high chemical activity and this must be taken into consideration in all experiments.

## APPARATUS PROBLEMS

Most commercial gas chromatographs are intended for use at temperatures not higher than 450–500°. EUSTON AND MARTIN<sup>2</sup> described a gas chromatograph with a column heated up to 1000°. However, we could not find any information concerning the applications of this instrument in recent publications.

An American patent<sup>3</sup> on the gas chromatographic purification of compounds boiling at temperatures up to 3000° has been published. But neither the actual apparatus nor the methods were described.

*Detectors*

Detection of inorganic vapours at red heat temperatures and higher is a most difficult problem. Most of the known gas chromatographic detectors are located in a thermostat and consist of gas-tight hollow metal blocks forming the basis of an electrical condenser (*i.e.* the electrodes are isolated by electrical insulators), joined to the columns by means of threaded junctions.

Even the manufacture of a simple gas-tight threaded junction to operate at temperatures of about 800–1000° involves difficulties, since such a junction is quickly oxidised and destroyed in the air. In the absence of oxygen, the diffusion welding of metal surfaces is observed. At higher temperatures, the problem is still more complicated, since refractory metals due to recrystallisation become very brittle at high temperatures. All the nonmetallic refractory materials are also brittle and are of little use for this purpose, while the manufacture of the column with a detector as one unit is inconvenient and not always possible. No less difficult a problem is the manufacture of gas-tight electrical insulators for operation at very high temperatures. The use of external (location outside the thermostat) detectors, such as the flame ionisation detector, flame photometer etc. entails heating the inlet tubes to the detector to the high temperature, since the vapours of high boiling point substances condense very rapidly even with very little cooling. Finally, it should be noted that many of the usual principles of detection barely operate or do not apply at super-high temperatures.

*The flame ionisation detector.* It is believed that the flame ionisation detector is unsuitable for the detection of inorganic substances. However according to MARTIN AND EUSTON<sup>2</sup>, stannic and ferric chlorides can be detected with this detector. Unfortunately, this information is very scant and a more detailed investigation is necessary.

In our tentative investigation, it has been found that Zn, Cd and some inorganic halides can be detected with a flame ionisation detector of the type as described by EUSTON AND MARTIN. However, heating of the inlet tube and metal detector jet, even up to 700°, causes a considerable increase in the noise level. With subsequent increases of temperature, the noise rapidly rises, the signal-to-noise ratio rapidly decreases, and detection becomes impossible. In addition, the metal oxides formed in the hydrogen flame are deposited on the detector electrodes which causes the detector parameters to deteriorate.

*The flame-thermocouple detector*<sup>4</sup>. According to our data, this detector is suitable for detecting combustible inorganic substances such as metal vapours. But we could not obtain good sensitivity and signal-to-noise ratio.

*The gravimetric detector.* This detector described by BEVAN AND THORNBURN<sup>5</sup>, is in principle suitable for detecting any inorganic substances at any separation temperature. However, we have found that metal vapours are instantly oxidised in the presence of air and higher boiling oxides are partially deposited on the inlet tube, thus choking the outlet from the chromatograph. It is therefore necessary to protect the outgoing vapours adequately from air, oxygen and moisture. Quantitative detection is also hindered by rapid condensation of high boiling inorganic vapours in the form of a highly dispersed mist which is only with difficulty retained by a trap.

*The thermal conductivity detector.* This is apparently useful at very high temperatures. But the design and manufacture of a superhigh temperature katharometer presents certain difficulties such as: the problem of the stability of the electrical insulators at high temperatures; the solution of the problem of filament sagging; and the protection of the filaments from corrosion, etc.

*The gas density balance.* This is rather more suitable for use at superhigh temperatures than the katharometer, since the filaments of this detector do not come in direct contact with corrosive vapours due to separated components. In addition, the electrical part of the detector may be removed external to the heated thermostat into the cold zone<sup>6</sup>.

*Pneumatic detectors<sup>7,8</sup>.* The pneumatic signal of a drossel or diaphragm detector may be brought out of the heated zone through a hollow tube and then converted into an electrical signal outside the thermostat by means of the usual recording manometer. This permits the successful use of such detectors at superhigh temperatures, since the electrical insulation problem can be avoided here. In our experiments with these detectors good results have been obtained<sup>9</sup>. The stainless steel diaphragm detector used at temperatures up to 1100°, is shown in Fig. 1.

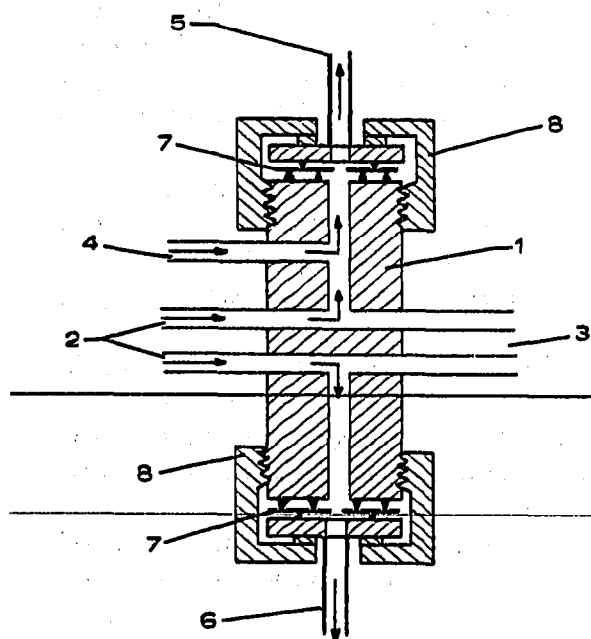


Fig. 1. Diaphragm detector. 1 = body; 2 = admission of blowing gas; 3 = pneumatic signal outlet; 4 = column carrier gas inlet; 5 = carrier gas outlet; 6 = blowing gas outlet; 7 = diaphragms; 8 = nut.

*Other detectors.* A successful attempt to detect Zn and Cd vapours at 300° by means of a discharge detector has been described<sup>10</sup>. However, the use of any ionisation detector at red heat or higher temperatures must be complicated by noise due to thermo-electronic emission. In addition, there are the already mentioned difficulties presented by high temperature in hermetically sealing the electrical insulators and by the decrease in the insulator resistance. Apparently, good results may be expected when using such detectors as the flame photometer, the atomic absorption photometer, the emission spectrometer and possibly the mass spectrometer.

*Other apparatus and material problems*

*The thermostat.* The design of a gas chromatographic thermostat for use at temperatures up to some thousand of degrees with a thermostating precision within a few degrees involves no difficulties in principle. A number of commercial ovens for heating at the temperatures required are manufactured. The methods for increasing temperature stability are also well known.

*Introduction block.* Substances boiling at the temperature of red heat and higher are usually solid at room temperature. For the introduction of such samples into the superhigh temperature column, systems which are already known may be successfully used, for example the system described by BAILEY and coworkers<sup>11</sup>.

*Outlet block.* On leaving the column, the vapours of high boiling point inorganic substances rapidly condense; in addition, some of them (for example, metal vapours) can be oxidised immediately upon contact with air. As a rule, the boiling temperatures of the oxides are higher than those of the original metals, so the oxides stop up the outlet tube even when it is heated. Therefore the outlet block must be constructed in such a way that the outgoing vapours can condense in a chamber of relatively large diameter without access to air.

*Columns.* Tubes made from refractory materials or metals can be used as columns. In the latter case, it is necessary to protect the columns against the air/oxygen. At relatively low (up to 1100–1200°) temperatures quartz and stainless steel tubes can be used.

*Adsorbents and solid supports.* At temperatures up to 700–800° silica gel, alumina and activated charcoal may be used as adsorbents for gas–solid chromatography. At higher temperatures, graphite, carbon blacks and possibly metal oxides, borides, nitrides and other refractory materials are used. Ordinary gas chromatographic solid carriers, for example Celite-545, Chromosorb W etc. can be used with liquid phases such as fused salts at temperatures up to 1000°. At higher temperatures, refractory oxides of aluminium, beryllium, zirconium, etc. are used. Metal or metallised solid supports seem to be most suitable when fused metals are used as stationary phases.

*Carrier gases.* Argon and helium, free from oxygen and water vapour, and in some cases nitrogen and hydrogen can be used as a carrier gas.

~~Some experimental results obtained with the use of the superhigh-temperature gas chromatograph designed in our laboratory are presented below.~~

#### CHROMATOGRAPHIC BEHAVIOUR OF SOME HIGH BOILING INORGANIC SUBSTANCES

The gas chromatograph with a diaphragm detector intended for temperatures up to 1100° was used throughout this work (Fig. 2). A vertical crucible oven with

an additional thermostating arrangement was used as a thermostat. The thermostating precision was  $\pm 2^\circ$ . The detector includes two stainless steel diaphragms, 0.15 mm thick (the diameter of the hole was 0.2 mm). The sensitivity of such a device

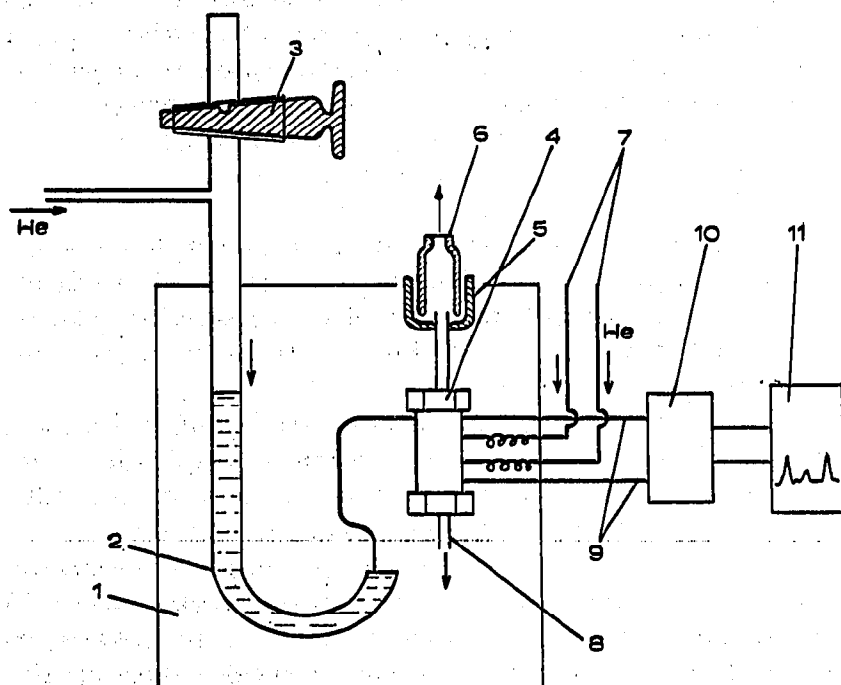


Fig. 2. Scheme of superhigh temperature gas chromatograph. 1 = thermostat; 2 = packed column; 3 = sample introduction block; 4 = detector; 5 = sample outlet block; 6 = quartz tube for condensation of outgoing components; 7 = admission of blowing gas; 8 = standard gas outlet; 9 = outlet of pneumatic signal; 10 = differential recording manometer; 11 = recorder.

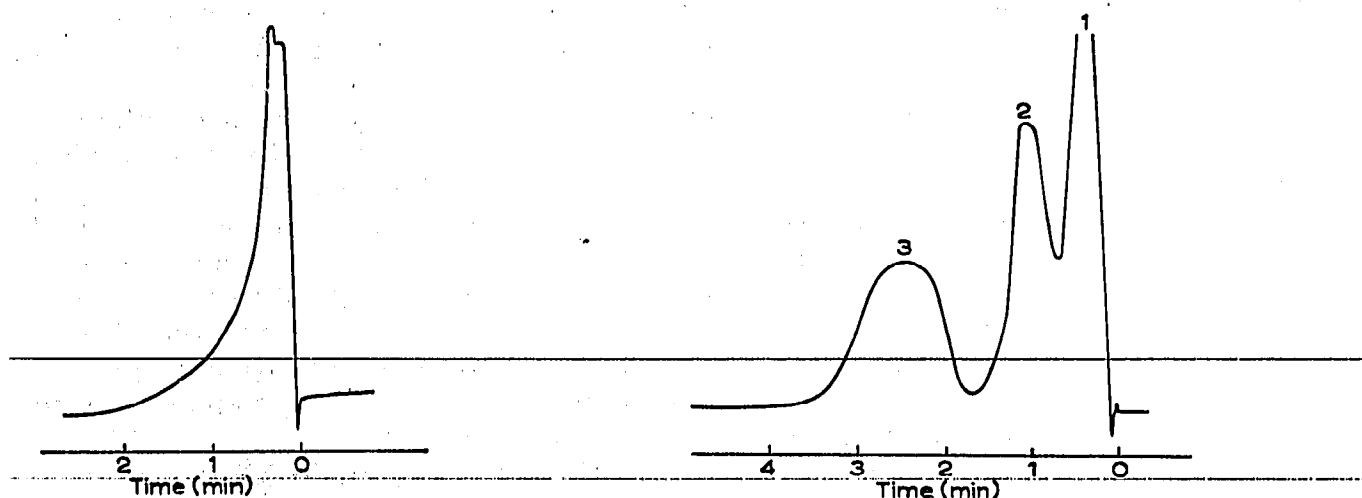


Fig. 3. Typical distorted peak of cadmium. Stainless steel column: I.D. 6 mm; packing: alumina (0.25–0.5 mm), length of packed layer 20 cm, temperature  $800^\circ$ , carrier gas (helium) velocity 60 ml/min.

Fig. 4. Chromatogram of mixture of Zn, Cd and Hg. Stainless steel column: I.D. 6 mm, packing: graphite (0.25–0.5 mm), layer length 20 cm, temperature  $800^\circ$ ; carrier gas (helium) velocity 60 ml/min; 1 = Hg; 2 = Cd; 3 = Zn.

for detecting cadmium at  $800^{\circ}$  (carrier gas (helium) velocity of 100 ml/min) was about 1200 mV ml/mg.

U-shaped and coiled quartz and stainless steel tubes (6–8 mm in diameter) were used as columns.

#### *Gas-solid chromatography*

Firebrick, quartz, silica gel, activated charcoal, Celite-545, Chromosorb W, alumina, calcium oxide, calcium fluoride, free iron, free copper and graphite of spectral purity were investigated as adsorbents for the separation of the some chemical elements and inorganic halides.

Cd, Zn, Hg, Na, K, S, Se,  $TlCl$ ,  $CdI_2$ ,  $PbCl_2$ ,  $SnCl_2$  were used as the components to be separated. It was found that Cd and Zn are partially separated at  $700$ – $900^{\circ}$  on many adsorbents<sup>9</sup>, but in most cases the peaks were distorted (Fig. 3). Various impurities present in the adsorbents seem to affect their properties to a considerable extent. Thus commercially activated charcoal absorbs Zn vapours irreversibly at  $850^{\circ}$ . However, after washing the charcoal with hydrochloric acid, this absorption was not observed. The best results for Zn, Cd (and Hg) separation were obtained with a graphite packing. The peaks have a good shape, and good reproducibility was observed (Fig. 4). We failed to obtain peaks for K and Na, since these metals absorb irreversibly on all investigated materials at  $700$ – $1000^{\circ}$ . Sulphur and selenium vapours have different retention values on silica gel and graphite at  $450$ – $600^{\circ}$ \* and give symmetrical peaks. However, attempts to separate mixtures and alloys of these elements were unsuccessful, obviously as a result of the formation of selenium sulphides (Fig. 5).

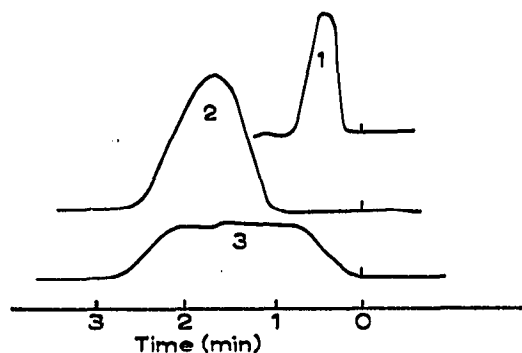


Fig. 5. Behaviour of sulphur and selenium in gas-solid chromatography. Quartz column: I.D. 8 mm, packing: silica gel, layer length 20 cm, temperature  $500^{\circ}$ , carrier gas (helium) velocity 80 ml/min. 1 = pure sulphur, 2 = pure selenium; 3 = S + Se alloy (1:1) (the same picture was observed on introducing a mechanical mixture of sulphur and selenium).

As a rule, inorganic halides could not be separated on the adsorbents under investigation. In many cases, partial or complete absorption of such components was observed, especially in the experiments with stainless steel columns.

#### *Gas-liquid chromatography*

Irreversible absorption of  $SnCl_2$  and  $PbCl_2$  at  $700$ – $1000^{\circ}$  in a 20 cm column

\* These experiments were carried out with a quartz device.

TABLE I

## QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF Zn-Cd BINARY ALLOYS

Separation conditions: stainless steel column (0.8 × 100 cm), packing: graphite of spectral purity (0.5-1 mm), carrier gas (helium) velocity 30 ml/min, temperature 800°, diaphragm detector.

Sample size (mg)	Cd containing (%)		Rel. error (%)	Zn containing (%)		Rel. error (%)
	Calc.	Found		Calc.	Found	
50	0.47	0.48	+2	99.53		
40	0.97	0.97	0	99.03		
20	1.90	1.93	+1.6	98.10		
10	3.40	3.30	-3.0	96.60		
10	6.90	7.10	+2.8	93.10		
5	32.0	32.9	+2.7	68.0	67.9	+1.9
5	34.3	34.6	+0.9	65.7	64.8	-1.4
5	42.0	43.4	+3.2	58.0	57.2	-1.4
5	79.8	81.2	+1.8	20.2	21.1	+4.3

containing 50% KCl on Chromosorb W (80/100 mesh) was observed. TlCl and TlBr at 850° give symmetrical peaks with appreciable retention. CdI<sub>2</sub> gives a peak with very weak retention. After introduction of a mixture of TlCl and CdI<sub>2</sub> in this column, two well separated peaks at 800° were recorded. Zn was irreversibly absorbed on this column at temperatures up to 950°, and Cd gives a broad peak with appreciable retention.

These results are tentative; it is obvious that chemical conversion of compounds in the column is possible\* and careful investigation of the outgoing components from the columns is necessary.

## DIRECT QUANTITATIVE ANALYSIS OF SOME ALLOYS

We have investigated the possibility of using superhigh temperature gas chromatography for the direct gas chromatographic determination of Cd and Zn in binary alloys. Analysis was carried out at 800° on a graphite column by means of the absolute calibration method. Pure Zn and Cd were used for plotting the calibration curves. Each alloy was analysed in three replicate samples. The results obtained are presented in Table I.

From Table I, it is evident that the direct gas chromatographic analysis of alloys containing Zn-Cd gives satisfactory quantitative results. It seems that other alloys could also be analysed in this way.

From the above it can be seen that the gas chromatographic separation of high boiling compounds at temperatures greatly exceeding the usual ones for gas chromatography is quite possible. However, the limits of applicability of superhigh temperature gas chromatography for analysis, preparative purification of compounds and physico-chemical purposes are not clear enough at present and further investigation is necessary.

\* For instance, when introducing CdI<sub>2</sub> into the column containing KCl, the generation of I<sub>2</sub> was observed.

## ACKNOWLEDGEMENT

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