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HIGH-PERFORMANCE EMITTERS FOR USE IN A SURFACE IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY

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SUMMARY

An attempt has been made to find good emitter materials for use in a surface ionization detector for gas chromatography. The sensitivity, detectability and stability characteristics were examined for ten refractory metals such as Pt, Ir and Re using tri-*n*-butylamine as a test compound. Of these materials, iridium is the best in terms of detectability. It not only provides six times the detection ability of Pt, but also shows good stability, reproducibility and durability.

INTRODUCTION

The surface ionization detector has recently been developed for gas chromatography¹. It utilizes a platinum filament emitter which is heated electrically. The emitter connected to the ion collector is positioned 2 mm above the nozzle of the carrier gas exit, which is maintained at a positive potential with respect to the collector. This detector is extremely sensitive to organic compounds such as tri-*n*-butylamine (TBA) which dissociates to species having low ionization potentials. It can be operated in any kind of carrier gas and the addition of air (oxygen) to the detector environment improves the performance.

Studies of the response of this detector have shown that the ionization mechanism involves positive ionization of organic species² generated on the hot surface. The molecules being detected decompose on the hot surface into radicals which have lower ionization potentials (IPs) than the molecules and are ionized and partially desorbed. The ion current of the secondary species (*s*) is dependent on the surface temperature, *T* (ref. 3)

$$i_s(T) = \frac{n \cdot Y_s(T)}{1 + g_0/g_+ \cdot \exp\left(\frac{IP - \varphi}{kT}\right)} \quad (1)$$

where n is the number of molecules impinging on the surface, $Y_s(T)$ is the yield of chemical reactions on the surface, ϕ is the work function of the surface and g_+/g_0 is the ratio of the statistical weights of the ions and the neutral species. The total ion current is $I(T) = \sum_s i_s(T)$.

Although the principal of the detector has been established, there are many factors which require investigation in order to further the understanding of the detector characteristics as well as improve its operation:

(1) The previous study was made with a platinum emitter which showed good performance. However, it is not known whether platinum is the most suitable material for this purpose. The first priority is therefore to find the emitter material which gives the best response under the desired operating conditions.

(2) The structure and positioning of the emitter.

(3) The effect on the performance of changing the gaseous environment in which the emitter is placed.

(4) The stability, reproducibility and durability.

We have investigated ten types of metals as the emitter material, chosen primarily because of their refractory properties. The response and performance characteristics of these emitters was examined in various gaseous environments. Emphasis is placed on a comparison of the relative ionization abilities of the emitters. In addition, some information on their lifetimes under the optimum operating conditions is presented.

EXPERIMENTAL

Instrument

The laboratory built detector was used with a Shimadzu Model GC-7A Pr F gas chromatograph. The detector components have been described previously¹. A glass column (3 × 2.6 mm I.D.) containing 10% Apiezon L + 5% potassium hydroxide on Chromosorb W (80–100 mesh) was used. Nitrogen and helium were tested as carrier gases. Samples were prepared using acetone as a solvent, with TBA as the test compound.

Procedure

The emitter was formed from the ten materials in various shapes and then fixed to the ion collector. The materials tested (The Japan Lamp Industrial Co., Tokyo) are listed in Table I. After installation, all the emitters were conditioned by passing sufficient current to reach a temperature of 1200°C while introducing 20 ml/min of air to the surface.

All the emitters were heated to a satisfactorily high temperature well below the respective melting points (at least 300°C) in order to study the effect caused by varying the emitter surface temperature. The emitter temperature was measured by an optical pyrometer Model 760 (Chino Works, Ltd, Tokyo).

None of the column or operating parameters was changed during the study. TBA gave symmetrical peaks. Thus, the peak areas were obtained from the product of the height and width at half-height, and expressed in terms of Coulombs (C) divided by the sample amount (g). Therefore the sensitivity as defined by Patterson⁴

TABLE I

SENSITIVITY AND DETECTION LIMIT FOR THE EMITTER MATERIALS USING TBA AS A TEST SAMPLE

<i>Emitter material</i>	<i>Work function*</i> (eV)	<i>Melting point*</i> (°C)	<i>Sensitivity**</i> (C/g)	<i>Detection limit***</i> (g/s)	<i>Emitter temperature§</i> (°C)
Pt	5.65	1774	1.58	$1.0 \cdot 10^{-14}$	650
Rh	4.98	1966	$2.7 \cdot 10^{-2}$	$1.6 \cdot 10^{-13}$	<650
Mo	4.6	2620	$2.5 \cdot 10^{-1}$	$5.4 \cdot 10^{-14}$	<650
Ir	5.27	2450	6.52	$1.7 \cdot 10^{-15}$	<650
Ni	5.15	1453	$2 \cdot 10^{-2}$	$2.1 \cdot 10^{-13}$	<650
Co	5.0	1495	$3.4 \cdot 10^{-3}$	$1.3 \cdot 10^{-12}$	<650
Re	4.96	3180			
W	4.55	3410			
Ta	4.25	3000			
Pd	5.17	1552			

* These data are taken from ref. 8.

** Measured under the optimum condition for the detection limit.

*** Minimum detectable amount at a signal-to-noise ratio of 2.

§ Temperature for the minimum detectable amount.

was used as one of the criteria for characterization. Measurements of noise were made with a strip-chart recorder and expressed in Amperes. The detectability was calculated as twice the noise divided by the sensitivity.

The stability of the detector with different emitters was investigated by measuring the background current and the noise level. The variation in the background current over 1 h was studied after determining the optimum heating current which gave the best detection limit. Some of the emitters were subjected to a reproducibility test by injecting TBA over a 1-h period.

RESULTS AND DISCUSSION

Sensitivity

Length and position of the emitter. In preliminary studies, we found that the position and length (surface area) of the emitter effect the sensitivity characteristics. The emitter length vs. response characteristics were investigated using a platinum filament with a diameter of 0.25 mm. The filament was shaped to a coil of diameter 3 mm, the number of turns of which determined the length of the emitter. The results for TBA are shown in Fig. 1. The signal increases with the length of the emitter and levelled off at about eight turns. The position of the emitter had no significant effect on the sensitivity, particularly for a highly coiled emitter.

Gaseous environment around the emitter. It is well known that, in surface ionization (SI) mass spectrometry, the addition of oxygen raises the work function of the heated SI emitter⁵ because of the oxidation on the surface, while organic compounds result in a decrease in the work function due to carbonization of the surface⁶, *i.e.*, poisoning of the emitter.

To study the effect of the introduction of air, emitters made from Pt, Ir and

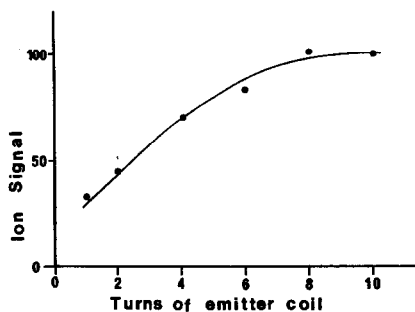


Fig. 1. Dependence of the ion signal on the length of the platinum emitter. Emitter temperature: 650°C. Sample: 0.1 ppm TBA in acetone. GC conditions: column temperature, 150°C; 30 ml/min nitrogen carrier gas mixed with air at 20 ml/min.

Mo were prepared in air (oxygen) using the procedures described in the Experimental section. Presumably the surface of the emitter is oxidized to M_xO_y compounds during this process. When a 1- μ l test sample of 1 ppm TBA in acetone was injected repeatedly into these fresh emitters under a 30 ml/min flow of helium and without any other gas, the signal gradually decreased. This trend was found for all the emitters studied, and may be interpreted as the removal of oxygen from the oxidized surface due to reactions between the metallic oxides and the organic compounds on the hot emitter surface. This explanation is consistent with the mentioned phenomenon in SI mass spectrometry.

It can be concluded that an oxidized emitter should be used in order to improve sensitivity and stability and to prevent poisoning. Such an oxidized emitter can be obtained if air (oxygen) is added to the emitter surface from another gas line. Experience has shown that at least 10 ml/min air is sufficient to prevent poisoning of the emitter in the case of helium as carrier gas, as will be discussed later.

A very slight difference was observed in the response when the detector was operated in helium rather than nitrogen as the carrier gas. This result may be attributable to the greater thermal conductivity of helium in comparison to nitrogen which causes a different surface temperature and hence a shift in the response. With the helium carrier at least 10 ml/min air are required to prevent poisoning, which is much more than with nitrogen as the carrier. At present, we do not have an explanation for this observation. In spite of these differences, it can be concluded that the detector is insensitive to the nature of the carrier gas; the sensitivity with helium or nitrogen as carrier is practically identical under optimum conditions.

Emitter material. Fig. 2 illustrates the effect on the response caused by varying the emitter surface temperature, T , for six kinds of emitter materials. All the emitters were formed into single loops from wire of 0.25 mm diameter and then assembled into the detector housing so as to give the same length (area) and position. A 30 ml/min flow of carrier gas (nitrogen) was mixed with the air at 20 ml/min. Since these emitter conditions were carefully controlled, it is certain that the observed large differences in $I(T)$ behaviour are due to the differences in the properties of the emitter materials.

Results could not be obtained for W, Re and Ta which were burnt out after

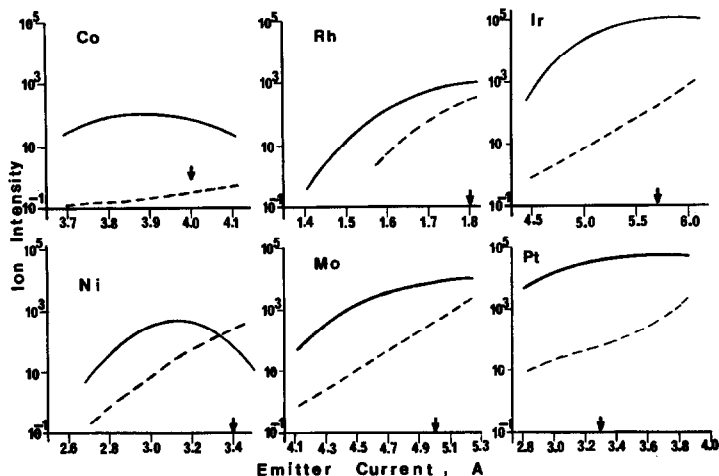


Fig. 2. Dependence of the TBA response (solid line) and background current (dotted line) on the emitter heating current. The operating conditions are the same as in Fig. 1. The arrows indicate the temperature (ca. 650°C) above which incandescence can be perceived.

several hours even at emitter temperatures of much less than 650°C. Palladium yielded no response at all, and is thus also omitted from Fig. 2. Fig. 2 shows that both the signal, $I(T)$, and the background current, i_b , increase with the heating current (temperature) and i_b varies widely from material to material. The I vs. T curves were bell-shaped for Co and Ni, but with the other emitters the ion signal increased with the heating current and levelled off at saturation values.

The maximum sensitivity for TBA occurs at a different emitter heating current from metal to metal, decreasing in the order Ir, Pt, Mo, Ph, Ni, Co, the value for Ir is times higher than for Pt, which is six times higher than for Mo. The response for cyclohexene followed the same order as that for TBA.

At first we believed that the wide variations in sensitivity could be related to the work function of the emitters, but no relationship has been found (Table I). This suggests that at the high surface temperature the emitter surface converted to an other oxide compound. Presumably the different work functions of the new chemical materials formed on the emitter surface is responsible for the wide variations in sensitivity.

Using Mo, Ir and Pt as emitters, the sensitivity for acetone was measured⁴. Both Mo and Ir are as specific as Pt, as previously reported. The selectivity, defined as the sensitivity ratio, $S(\text{TBA})/S(\text{acetone})$, was $4 \cdot 10^4$ and did not differ significantly among these three emitters.

Detectability

Since the emitters usually showed similar detectabilities and sensitivities (Table I), we picked the three best emitters in terms of sensitivity for the detectability study. Fig. 3 shows the dependence of the signal-to-noise ratio, S/N , on the emitter current, obtained with nitrogen as the carrier gas mixed with air. It should be pointed out that careful adjustment of the heating current is required in order to detect trace

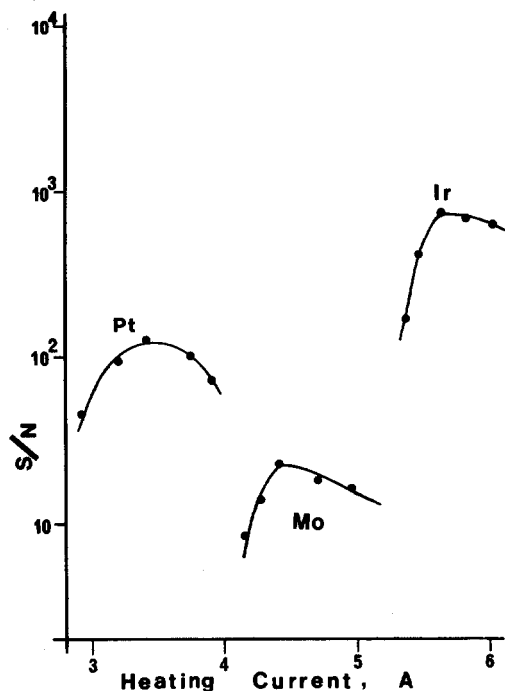


Fig. 3. The signal-to-noise ratio, S/N , vs. heating current for various emitters. The operating conditions are as in Fig. 1.

components. Again the iridium emitter provides the best detectability among the three, partly because it gives a lower noise level. There is no obvious explanation for the lower noise characteristics of this emitter.

Stability

Baseline stability. A previous paper¹ reported the stability of the baseline of a surface ionization detector with a hot platinum emitter, noting that about 60 min from switching-on the emitter platinum were required to achieve a stable baseline even at a very low current of $2 \cdot 10^{-11}$ A.f.s. However, the data were obtained for an emitter which was not well defined as regards the initial conditioning and its subsequent usage.

In the present work the thermionic stability with time was investigated in detail for the iridium emitter, which gives the best performance. In the initial conditioning stage with 20 ml/min air after mounting a new iridium emitter in the detector envelope, the background current and the noise level are highest. The large background current is probably attributable to the appearance of Na^+ and K^+ from Na and K as impurity atoms in the iridium material⁷. After heating for 24 h, the background current decreases to *ca.* 1/10 and becomes stable, remaining practically unchanged during the subsequent analytical use. In repeat experiments a stable baseline at a current of $2 \cdot 10^{-11}$ A.f.s. was obtained within half an hour of switching on.

Reproducibility. The effect of the analyte on the stable operation of the detector was investigated. It might be expected that the temperature of the emitter surface

would change with the analyte compounds, caused by the thermal conductivity effect¹. Based on the experimental I vs. T curves shown in Fig. 2, which have a wide flat portion at higher temperatures, no significant effect was apparent.

The second possibility is a change in the surface properties, brought about by alteration of the surface composition due to complex reactions between the surface material and the organic analyte. However, as already mentioned, such a poisoning of the emitter can be prevented if additional air flow is supplied to the detector. For the iridium emitter placed in air, reproducibility tests were performed by replicate injections (ten times) of the 2.6- μ l standard sample containing 0.1 ppm TBA. Good reproducibility was achieved: the standard deviation was 1.25 and the coefficient of variation was 1.1% using peak heights (mm).

Durability. If Ir is heated at a current of 6.1 A (ca. 1200°C) in the air, it will burn out in 2 days. However, at a heating current of 5.6 A (less than 650°C), which gives the highest detection limit, and at a carrier gas (helium) flow-rate of 40 ml/min mixed with 20 ml/min air, a single emitter can be used continuously for more than 3 months and with no significant drift in sensitivity. The platinum and molybdenum emitters are also capable of withstanding more than one month's analytical use provided they are not heated excessively.

CONCLUSIONS

This study has demonstrated that of the ten materials examined Ir provides the best performance as an emitter for use in a surface ionization gas chromatographic detector, as regards the sensitivity and the detection ability: the sensitivity is 6.52 C/g and the minimum detection limit is $1.7 \cdot 10^{-15}$ g/s for TBA. Also it has very good stability and a low noise level in the presence of air.

There is little difference in performance between the previously studied platinum emitter Ir. Platinum is less expensive and more easily available than Ir. Thus it should also be recommended.

The detector can be built in the laboratory if the gas chromatograph employed is equipped with a conventional flame ionization detector: the iridium (or platinum) emitter can be mounted in the gas flow path through the hole of the envelope which is used for igniting the flame.

Since the further development of this detector seems to be impossible without investigating its applicability, we have already started to explore this field. Preliminary results suggest that either an iridium or platinum emitter may be successfully used for the sensitive gas chromatographic analysis of alkylamines, ethanolamines, nitrosamines, hydrazines, aromatic hydrocarbons, etc.

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