Characterization of a gas chromatographic surface ionization detector based upon hyperthermal positive surface ionization

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Abstract

Characterization of a gas chromatographic surface ionization detector based upon hyperthermal positive surface ionization is described. The newly developed detector consists of a supersonic free-jet nozzle and the high-work-function surface of ReO_2.

This detector, which is highly sensitive in response to all organic compounds, can be operated as a universal detector. There will be some additional selectivity toward some species having low ionization energy, but this will be much less than with conventional surface ionization detection. The minimum detectable amount of toluene is around 10^{-12} g/s with linearity greater than 10^4.

1. Introduction

Surface ionization detection (SID) is a very sensitive and selective method in the gas chromatographic (GC) detection of organic compounds [1]. The response of the SID detector varies with the ionization energy (IE) of the sample organics and the work function (ϕ) of the surface, to the extent that there is no response to some organic molecules with high IEs.

Recently, a new approach to gas chromatographic SID was reported by Amirav [2]. This new SID is based upon the finding that when the organics are provided with molecular kinetic energy up to ca. 10 eV, surface ionization ef-

ficiency is greatly enhanced. The molecular kinetic energy is obtained in a supersonic free-jet expansion of the heavy organic molecules seeded in hydrogen (or helium) carrier gas through a supersonic nozzle. This ionization process may be termed hyperthermal surface ionization (HSI).

The purpose of the present study is: (1) to design and construct a new GC detector based on HSI, (2) to interface this to a GC and to show that the HSI signal is linearly related to the concentration of the sample, (3) to describe the optimal operational parameters for the use of this detector in GC, (4) to explain its detection mechanism, and (5) to compare its detection characteristics with those of the well-established flame ionization detection (FID) and photoionization detection (PID) techniques.
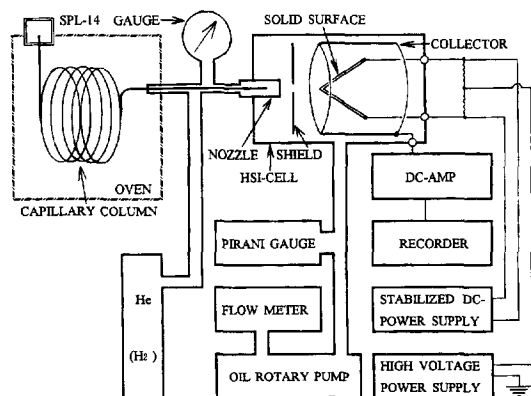
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Fig. 1. Schematic drawing of a "new surface ionization detector". The detector chamber is pumped by a 1000 l/min oil rotary pump. Typical operating conditions: the stagnation pressure, with helium gas as a seeding gas, 800 Torr; detector-chamber pressure 0.06 Torr; further see Table 1.

2. Experimental

2.1. Design of detector

The "new SID" detector is shown schematically in Fig. 1. Typical examples of the instrument parameters are given in Table 1. The detector comprises (1) a ceramic nozzle, (2) a shield plate disk, (3) a high-work-function surface, (4) an ion collector, and (5) a vacuum system. The detector's vacuum chamber was pumped by a 1000 l/min oil rotary pump (EC-602, ULVAC) alone, and the background pressure [P_b (Torr)], measured by pirani gauge (GP-1S, ULVAC), was around 0.06 Torr (8.0 Pa) under typical gas flow.

Table 1
Instrument parameters and typical operating conditions

E_k (kinetic energy)	1–10 eV
T_N (nozzle temperature)	≤1200 K
v (H$_2$ flow-rate for seeding)	100–200 ml/min
P_0 (stagnation pressure)	800–1600 Torr
P_b (background pressure)	1.0×10^{-2}–6×10^{-2} Torr
X_M (Mach disk distance)	3–8 mm
L (nozzle–surface distance)	5–10 mm
T_s (surface temperature)	300–1200 K
d (nozzle diameter)	80–100 μm

2.2. Supersonic free jet

Aerodynamic acceleration was used in order to obtain kinetic energy of 1–10 eV. In this technique, the molecular kinetic energy obtained (E_k) can be expressed as:

$$E_k^\infty = \frac{5}{2}\frac{M_h}{M_l}k_B T_N$$

$$E_k = E_k^\infty[1 - \exp(-\delta P_0 d)]$$

where E_k^∞ is the maximum value of E_k, M_h and M_l the molecular mass of the heavy and the light molecules in the beam, k_B the Boltzmann constant, T_N the temperature (K) of the nozzle, P_0 the nozzle stagnation pressure (Torr), d the nozzle diameter (cm), and δ a constant.

At a distance X_M (cm) from the nozzle, the Mach disk shock-wave structure would be formed:

$$X_M = 0.67(P_0/P_b)d$$

2.3. Nozzle

The ceramic nozzle forms a 100 (or 80)-μm diameter thin hole in a small ruby disk mounted on a 2 mm O.D. alumina tube, and can be heated electrically up to 1300 K at its 1.5 cm tip. The distance between the nozzle tip and the surface is about 10 mm.

2.4. Disk

The shield plate disk, with a 1-mm diameter hole at its center, could reduce the background and the noise level by more than two orders of magnitude. Background level is defined as the background current detected by the collector when the ionization filament and/or the nozzle heater are heated electrically, compared to that when both filament and heater are turned off. The noise level is the fluctuation of the background current.

2.5. Surface

The refractory metal foils, shaped like a mountain with two flat surfaces (each surface area,

1×10 mm^2) and fixed to the holder, were heated electrically up to 900°C, and biased +200 V against the collector electrode.

2.6. Collector

The ion collector is a concentric geometry of Faraday-cup-type electrode, which surrounds the metal surface.

2.7. GC system

The home-built detector was coupled to a Shimadzu GC-14A capillary gas chromatograph via heated transfer tubings. Helium was used as GC carrier, and a second stream of helium was added as a seeding gas at the outlet of the column to a level of 100–200 ml/min. Chromatography conditions were as follows. A fused-silica capillary column (Shimadzu FFS ULBON HRI, 25 m × 0.32 mm I.D., film thickness 0.5 μm) with a split/splitless injection system was used, at a He carrier gas rate of 0.7 ml/min and a split ratio of 100:1. The temperature program of the column oven was 40°C, 10 min hold, increased to 140°C at 2°C/min, then held at this temperature for 10 min. The temperature of the injection and detector ports was 200°C.

Sample molecules for study or calibration were reagent-grade alkyl alcohols and alkyl benzenes and hexane. The IEs of the test samples fall in the 8.8–10.5 eV range.

3. Results and discussion

3.1. Sensitivity optimization

There are a number of factors influencing the detection sensitivity. Of these, the kinetic energy (E_k) of the sample molecule, which is proportional to the nozzle temperature (T_N), and the surface temperature (T_s) are by far the most important. Investigation of the effect of the surface electrode bias voltage led to the conclusion that the ion signals saturate at a voltage higher than +200 V. Therefore, all the data reported were obtained at a bias voltage of +200 V.

Surface (emitter) material

The characteristics of ReO$_2$ and Pt as positive-ion-emitting surfaces were investigated. ReO$_2$ has long been used in surface ionization organic mass spectrometry [3], while Pt performs well as a surface material for conventional SID [4]. Preliminary study indicated that using ReO$_2$ gave a 20 times higher sensitivity than using Pt, and that the noise level was much the same for both surfaces. Therefore, ReO$_2$ is now being used exclusively.

Signal versus E_k

The response results for some organic compounds in C/g versus the nozzle temperature, along with background current and noise level in A, are given in a semilogarithmic plot (Fig. 2). The sensitivity varied exponentially with the kinetic energy (E_k) of the sample compound with all variables constant. This result is to be expected from the recent findings [5] that molecular kinetic energy has a dramatic effect in increasing the surface ionization yield.

From Fig. 2, relative sensitivity factors (RSFs) for sample molecules tested can be calculated, by dividing the detection sensitivity (C/g) of each sample molecule by that of n-hexane. The RSF for n-hexane is set at 1.00. Table 2 shows how the RSF can be affected by the nozzle temperature. From this table, we can see that the change in RSF with nozzle temperature is relatively slight, whereas the absolute detection sensitivities change dramatically, as seen in Fig. 2. Therefore, once the optimum nozzle temperature has been selected, this detector can be operated as a universal detector. There will be some selectivity toward species having low IEs, but this tendency will be much less than with conventional SID.

Signal versus T_s

Fig. 3 shows the results of sensitivity (in C/g) experiments as the surface temperature was increased from 700 to 1100°C, with background and noise level in A. The reason for the existence of a sensitivity maximum around $T_s = 900$°C may be that some chemical reactions in which chemical species with high IEs are formed begin
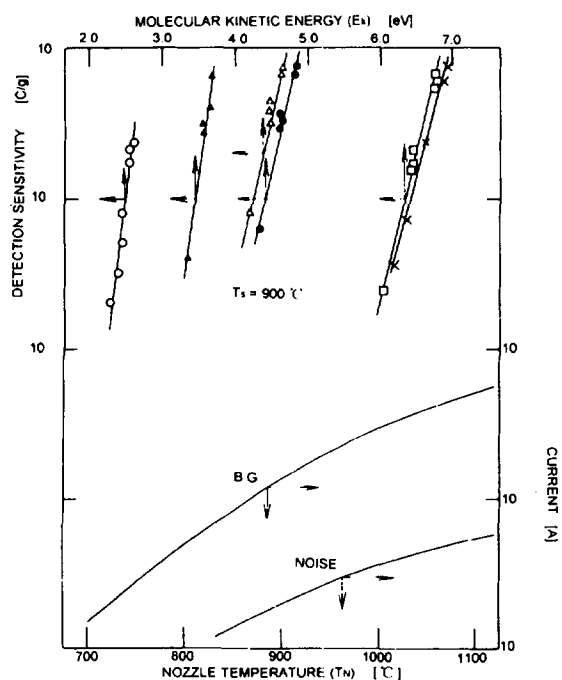
Fig. 2. Detection sensitivity as a function of molecular kinetic energy for various organic samples: (O) methanol, (▲) ethanol, (△) acetone, (●) 2-propanol, (□) cyclohexane, (×) n-hexane. Sample size, 10 ng; nozzle temperature, ≤1100°C; nozzle stagnation pressure, 800 Torr. The values for the kinetic energy, which was governed by the nozzle temperature, were calculated. Below: background signal (B.G.) and noise as a function of nozzle temperature. Background signal probably from surface alkali impurities that had been ejected by the accelerated molecules.

Fig. 3. Plot of surface temperature (T_s) versus signal current (detection sensitivity), noise level and background (B.G.) current at $T_N = 900°C$. Sample size, 10 ng in acetone. (O) Toluene, (▲) 2-propanol, (□) methanol, (△) o-xylene, (●) benzene.

around this temperature, causing the ionization yield to decrease.

The large background current shown in Figs. 2 and 3 is probably attributable to the formation of Na^+ and K^+ ions from Na and K impurity atoms in the surface material [5]. This assumption is consistent with the experimental fact that back-
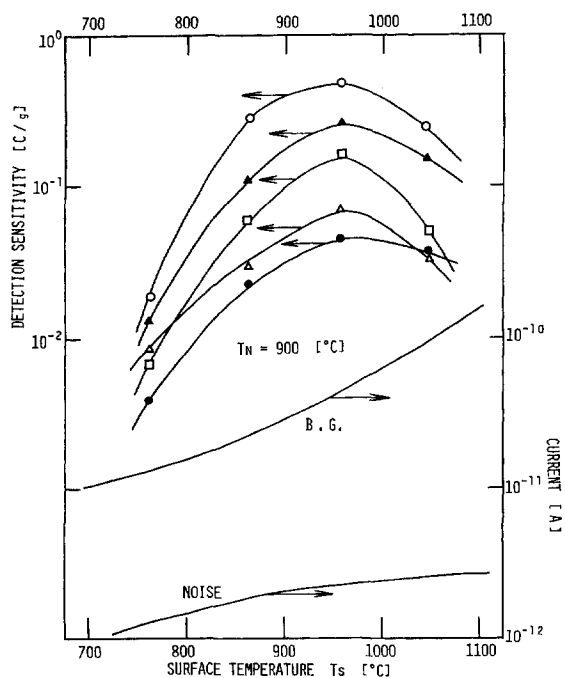
ground levels gradually decrease with time of operation.

The noise appears to be generated by other sources, such as the nozzle assembly, which also emits alkali ions, especially when it is heated. But the above-mentioned shield plate disk could reduce the background and the noise level dramatically.

The other important factor in terms of sensitivity is the fraction of jet gas flux intercepted by the surface. Therefore, we used a free-jet supersonic expansion (without collimation) on a

Table 2
Influence of nozzle temperature on relative sensitivity factor (RSF)

T_N (°C)	Methanol	Ethanol	Acetone	2-Propanol	Cyclohexane	n-Hexane
980	0.47	0.87	0.85	0.91	0.92	1.00
920	0.21	0.59	0.77	0.68	0.37	1.00
850	0.22	0.30	0.67	0.56	0.23	1.00

surface. The nozzle–surface distance would have an effect on the fraction of gas flux intercepted by the surface. When the distance was shorter, there was an apparent increase in the signal response. A very short nozzle–surface distance, however, caused a large increase in the noise level as well as the background current. In the following experiments, the nozzle–surface distance was kept constant at 10 mm so that the optimum signal-to-noise ratio could be provided.

In operating surface ionization organic mass spectrometry, an Re filament was placed in 2×10^{-5} Torr oxygen gas, which greatly enhanced the ionization yield [3]. The work function (ϕ) of ReO_2 is reported to be 6.4 eV, whereas that of Re metal is 4.9 eV [6], and the formation of ReO_2 contributes to increasing the ionization yield. In the present experiment, supersonic seeding gas (He), purity 99.8% (main impurity: air), was pumped down to 0.06 Torr of background pressure (P_b) in the HSI chamber. Under this experimental condition, the partial pressure of oxygen gas just amounted to ca. 2×10^{-5} Torr. Therefore, no additional oxygen supply was needed.

3.2. Performance characteristics

Performance was assessed on the basis of the criteria dynamic range, sensitivity, minimum detectable amount (MDA), and comparison with conventional SID.

Dynamic range

The dynamic range was investigated using methanol, benzene, and toluene as test compounds. Plotted on the vertical axis is sample peak area in C and along the horizontal axis is the sample introduction weight in g (Fig. 4). These data were obtained under the optimum conditions for the detection limit: a surface temperature of 900°C, which gives a background current of 4×10^{-11} A and a noise level of 10^{-12} A, and a kinetic energy of 3.4 eV (nozzle temperature 900°C). The response is linear over four orders of magnitude in sample amount. This dynamic range is somewhat smaller than that of FID (10^5–10^6) and of PID (10^7) [8,9].
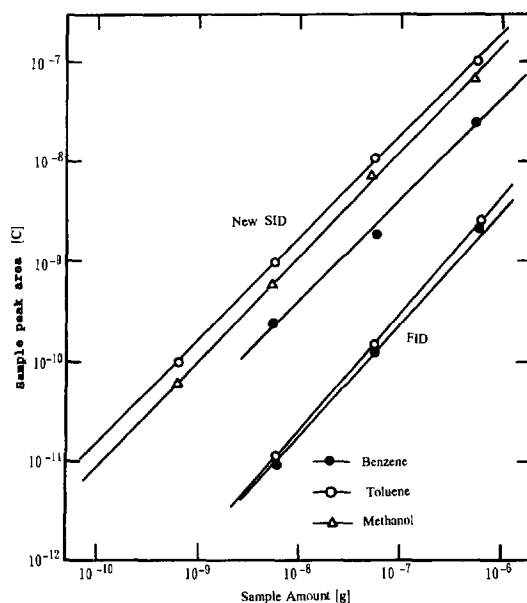

Fig. 4. Calibration plot for "new SID" and FID. "New SID" data were obtained under optimum conditions, i.e. surface temperature, $T_s = 900$°C; nozzle temperature, $T_N = 900$°C. (○) Toluene, (△) methanol, (●) benzene.

Sensitivity

Detection sensitivities were calculated as the linear regression slope of the above linear calibration plot. The sensitivity (S) of the detector can be expressed as Coulomb per gram of sample. For methanol, S was 0.24 C/g. This is 10 to 100 times better than that of FID, and is comparable to that of PID [8,9]. A sensitivity comparison with FID is presented in Fig. 5, which shows "new SID" and FID chromatograms for identical samples.

Selectivity

As already mentioned, the sensitivity of the detector is greatly dependent on the IE of the species as well as on the yield of the species generated through chemical reaction on the surface. Presumably, the relative sensitivity for different organics, which is easily determined by a comparison of the signal currents, varies over a wide range from sample to sample. Consequently, the selectivity of this detector, which is de-
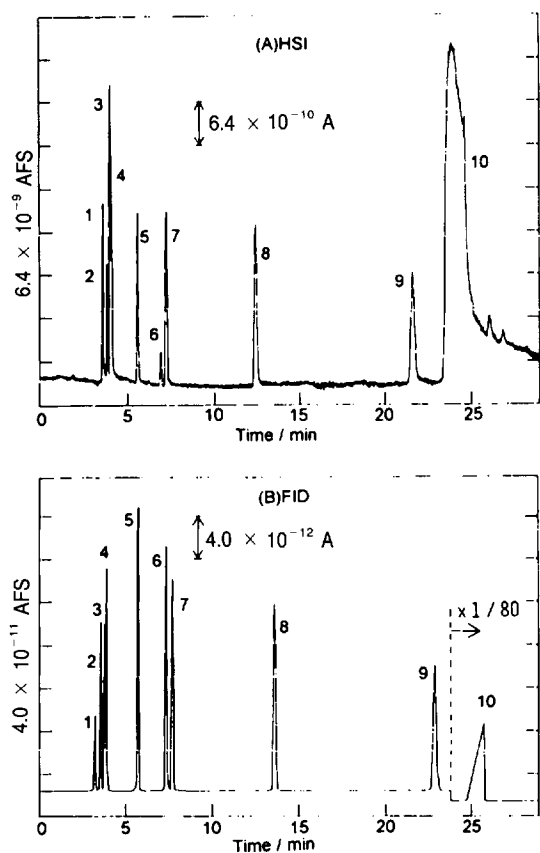
Fig. 5. Comparison between (A) "new SID" (with hyperthermal surface ionization, HSI) and (B) conventional FID. Both gas chromatograms: peaks 1–9, 50 ng sample; peak 10, 500 ng sample. Peaks: 1 = methanol, 2 = ethanol, 3 = acetone, 4 = iso-propanol, 5 = n-hexane, 6 = benzene, 7 = cyclohexane, 8 = toluene, 9 = m-xylene, 10 = o-xylene. "New SID" conditions: $T_N = 900°C$, $T_s = 900°C$. FID conditions: H_2 flow-rate, 30 ml/min; air flow-rate, 600 ml/min. Gas chromatographic conditions: Chemically bonded fused-silica capillary column (FFS ULBON HR1, 25 m × 0.32 mm I.D.); He carrier gas flow-rate, 0.70 ml/min; temperature program: 40°C, 10 min hold, increased to 140°C at 2°C/min, then held 10 min; injection port and detector port temperature, 200°C.

fined as the ratio of sensitivities, was determined and found to be:

$$S(\text{toluene})/S(\text{benzene}) = 1.2 \times 10^1.$$

MDA (noise)

As can be seen from Fig. 3, at higher surface temperature a decrease in the ratio of sample

peak intensity to the detector noise level occurs. This indicates that an optimum surface temperature has to be found for the highest detection limit. Generally favorable operation is achieved with a surface temperature of 900°C, which generates a noise level of 10^{-12} A at a nozzle temperature of 900°C. Under this optimum condition, the MDA at the signal-to-noise ratio of 2 was measured using toluene and was found to be 1×10^{-12} g.

3.3. Chromatogram

Fig. 5 shows examples of responses obtained when a mixture of alkyl alcohols, and aliphatic, alicyclic, aromatic hydrocarbons are chromatographed and measured by "new SID" and FID detectors. The lower trace shows these compounds as analyzed by the FID at an electrometer setting of 4×10^{-11} ampère full scale (AFS). The measurements in both the SID and FID modes were made under the optimum conditions for MDA. The upper trace shows the same sample analyzed by the "new SID" at setting 6.4×10^{-9} AFS.

By comparing the records from both detectors, it is found that: (1) SID operation provides significantly higher sensitivity than FID operation, even though the noise level for the former is about two orders of magnitude higher than that for the latter. (2) In the case of methanol, the detection capability of SID is 25 times higher than that obtained by FID. (3) The SID detector provides as a good resolution as the FID one, demonstrating that "new SID" responds rapidly enough to follow sharp capillary peaks. This is consistent with the fact that the use of a low-pressure or vacuum outlet technique for gas chromatography is widely associated with greater separation efficiency [7].

On occasion, the baseline also exhibits a sharp backward response at the peak tail. No completely satisfactory explanation for this unstable baseline has been formulated as yet. Attempts to find the cause have not been successful. The similar SID response appears sensitive to the analyte matrix, which could be a difficult problem to solve and result in poor quantitation.

4. Conclusion

The state-of-the-art in supersonic free-jet technique has been incorporated in a novel SID detector. Universal response using SID is a new development. Conditions have been found under which sensitivity is greatly increased by the introduction of a supersonic free-jet technique. All the response characteristics are consistent with a process of positive surface ionization. Therefore, a high-work-function surface is conducive to sensitive analysis, even for the "new SID".

In its present state of development, the response of "new SID" to most organic molecules including aliphatic alcohol is 100 times greater than the response obtained from the same compounds by conventional FID. The detector has a minimum detection capacity of 10^{-12} g/s, of toluene, a selectivity relative to hydrocarbons of $>10^1$, and a linear dynamic range of operation of $>10^4$.

Acknowledgement

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