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Surface ionization detector with a supersonic free jet for gas chromatography Some applications

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Abstract

A new design for a gas chromatographic surface ionization detector based upon hyperthermal positive surface ionization has been developed: There were two requirements: supersonic free jet nozzle and the high work function surface of Re-oxide. This detector, which is highly sensitive in response to all organic compounds, can be operated as an universal detector with an additional selectivity towards some species that have low ionization energy, but with selectivity to a much lesser degree than a conventional surface ionization detector. The minimum detectable amount of toluene is ca. 10^{-12} g/s with a linearity greater than 10^4. Some applications are demonstrated using three examples for the analysis of different formulations: (1), terpene mixture, (2), polycyclic aromatic hydrocarbon mixture and (3), alkyl alcohol mixture.

Keywords: ; Detection, GC; Surface ionization detection; Supersonic free jet nozzle; Terpenes; Polynuclear aromatic hydrocarbons; Alcohols

1. Introduction

Surface ionization detection (SID) is used in gas chromatography (GC) of organic compounds, which form their dissociative species at a low ionization energy (IE); it is a very sensitive and selective detection method [1]. The advent of SID in combination with GC dates back to the early 1960s, when Zandberg and Rasulev [2] described the nature of such a detection method. In 1984, Fujii and Arimoto [3] investigated SID with a hot platinum emitter, this work led to the first commercially available SID system from Shimadzu.

Recently, a new approach to GC–SID was reported by Danon and Amirav [4,5]. They reported on a new form of SID which is based upon the finding that when the organic compounds are supplied with kinetic energy to the surface, surface ionization efficiency is greatly enhanced. The molecular kinetic energy is obtained in a supersonic free expansion of the organic heavy molecule that has been seeded in hydrogen (or helium) carrier gas through a pinhole nozzle. This detection method is referred to as hyperthermal-SID.

Although the development of the new SID method, as described by Amirav [5], has been a major breakthrough in the analysis of trace quantities of compounds, the detector has not received the attention that would have been expected in view of its sensitivity, selectivity and versatility. This is proba-

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bly because of the limited number of investigations that have been carried out on this kind of detector, as it is not widely available.

Because the characteristics of this second-generation SID are still not widely understood, its development will be hindered without an investigation of its applicability; and this study was designed to explore the areas of application of SID. We began to study these new applications by choosing various organic compounds, with the understanding that the sensitivity of SID is dependent on (1), the kinetic energy of the sample molecules (nozzle temperature, T_n), (2), surface temperature (T_s), (3), the ionization energy (IE) of the species and (4), the yield of the species generated through chemical reaction on the SID emitter surface. In this work three types of compounds were investigated to provide a broader understanding of the potential applications of SID in chemical analysis.A comparison was made in terms of its detection characteristics with the well-established flame ionization detection (FID).

2. Experimental

2.1. Design of detector

A newly-designed SID was constructed, which is shown schematically in Fig. 1. The detector is comprised of (1), a ceramic nozzle assembly, (2), a shield over the nozzle assembly, (3), high-work-function filament surface and (4), ion collector, which are installed in the vacuum tube.

The technique of aerodynamic acceleration was used in order to obtain molecular kinetic energy in the range 1–10 eV. The organic molecules from the GC coupling which were seeded in a hydrogen or helium supersonic beam, enter the vacuum chamber through a ceramic nozzle [6]. The ceramic nozzle was a 80-mm thin hole in a small ruby disc mounted on a 2-mm alumina tube. It has been described in detail elsewhere [7]. The distance from the top of the nozzle to the surface is 5 mm.

In the vacuum chamber, the beam collided with a

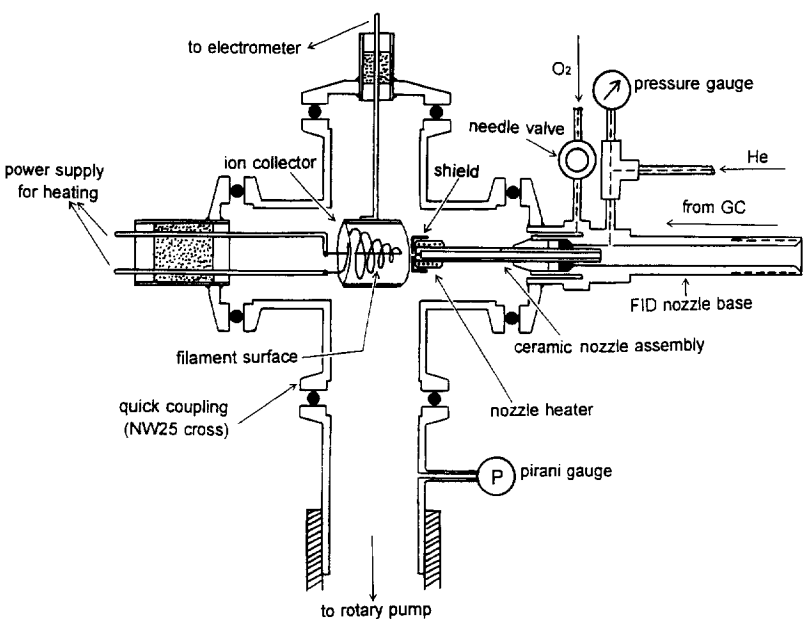

Fig. 1. A schematic drawing of a new surface ionization detector with the nozzle. The detector chamber is pumped by a 1000 ml/min rotary pump. The typical operating conditions are: the stagnation pressure with helium gas used as a seeding gas, 1000 Torr; pressure of the detector chamber, 0.06 Torr.

Re-oxide [8] or Pt surface [2] for efficient positive ion production. The Re-oxide surface was prepared separately in the presence of O_2 at the pressure of $1 \cdot 10^{-5}$ Torr (1 Torr=133.322 Pa) by electrical heating of the Re foil to ca. 1200 K for a few hours.

The ion collector is a cylindrical collector of Faraday cup-type geometry which surrounds the surface. The surface is always at a positive potential of 200 V against the collector electrode. There is a definite advantage in the cylindrical geometry of the detector design over that of the parallel plate, in terms of collection efficiency.

This laboratory-built detector was coupled to a Shimadzu G-23 capillary gas chromatograph (Kyoto, Japan). The FID and conventional SID systems used for comparison were commercial ones (Shimadzu, Models FID-17 and SID-12, respectively). A 25 m×0.32 mm I.D. chemically bonded fused-silica capillary column, FFS ULBON HR-1, was used with helium carrier gas at ca. 1 ml/min. This gas flow-rate was too small as a seed gas for supersonic jet operation. Therefore, another helium gas was added at the outlet of the column to the level of 150–200 ml/min. According to the explanation given above, it is obvious that the parameters of this system are related to each other and varied over a wide range. All the samples were purchased from Ieda Chemicals (Tsukuba, Japan), and used without further purification.

3. Results and discussion

3.1. Performance characteristics

Performance was assessed by using the criteria of dynamic range, sensitivity, selectivity, minimum detectable amount (MDA) and comparison with conventional SID. The values in the following sections are typical examples obtained with the newly-developed SID.

3.1.1. Dynamic range

The response is linear over four orders of magnitude in sample amount.

3.1.2. Sensitivity

Sensitivities were calculated as the linear regression slope of the linear (calibration) plots. The sensitivity (S) of the detector can be expressed as Coulomb per gram of sample. For toluene, S was 0.64 C/g. This was measured under the conditions that T_n=930°C (kinetic energy, E_k=11.9 eV) and T_s=900°C.

3.1.3. Selectivity

Presumably the relative sensitivity for different organic compounds, which is easily determined by a comparison of the signal current, varies in a wide range from sample to sample. Consequently, selectivity of this detector, which is defined as the ratio of sensitivity, was

$$S(\text{toluene})/S(\text{hexane}) = 5.3 \cdot 10 \quad (1)$$

3.1.4. Minimum detectable amount (noise)

Under optimum conditions, MDA at the signal-to-noise ratio of 2 was measured using toluene. The result ($1.6 \cdot 10^{-12}$ g/s) is listed in Table 1.

3.1.5. Comparison

In Fig. 2 a new-SID chromatogram of a series of *n*-alkyl benzenes is compared with conventional SID. By comparing both records, benzene (marked as 1) was barely detected in the conventional SID trace. With the new-SID, 5 ng toluene (2) will give almost a half-scale response at $6.4 \cdot 10^{-10}$ AFS. This is 800 times greater than conventional SID. It is clearly observed that the former is more sensitive and less selective than the latter. It should be noted, however, that the blank noise level for the new detector, a factor limiting MDA, is 100 times higher than for conventional SID, and therefore the new-SID provides a ca. 8 times better MDA for toluene, even though the sensitivity of new-SID is much higher than that of conventional SID.

3.2. Applications

3.2.1. Terpenes

A formulated monoterpene mixture (8 ng each) was tested. Fig. 3 shows chromatograms obtained from the analysis with two different detectors: (a)

Table 1
Comparison of the new SID with conventional FID and conventional SID

	New-SID	FID[a]	Conventional SID
Principle	Hyperthermal SI on Re-oxide	H_2/O_2 flame 2000°C plasma	Thermal SI on Pt
Sensitivity (S) (C/g of X[b])	0.64	0.015	$7.7 \cdot 10^{-4}$
MDA[c] (g/s of X)	$1.6 \cdot 10^{-12}$	$3 \cdot 10^{-12}$	$1.3 \cdot 10^{-11}$
Selectivity (S of X/S of hexane)	$5.3 \cdot 10$		$3 \cdot 10^{3}$
Linear dynamic range	10^4	$2 \cdot 10^6$	10^4

[a] Cited from Ref. [9]. X corresponds to n-propane.
[b] X corresponds to toluene as a test sample in the case of new SID and conventional SID.
[c] MDA = minimum detectable amount.

SID channel and (b) FID channel. The comparison reveals that the substance-specific characteristic is clearly demonstrated in the SID chromatogram; SID detects α-pinene most specifically among the other monoterpenes. The results illustrate a high sensitivity, with a detectability in the nanogram to sub-nanogram range. For α-pinene, SID provides a response of ca. 0.51 C/g with a sensitivity 46 times better than that of FID.

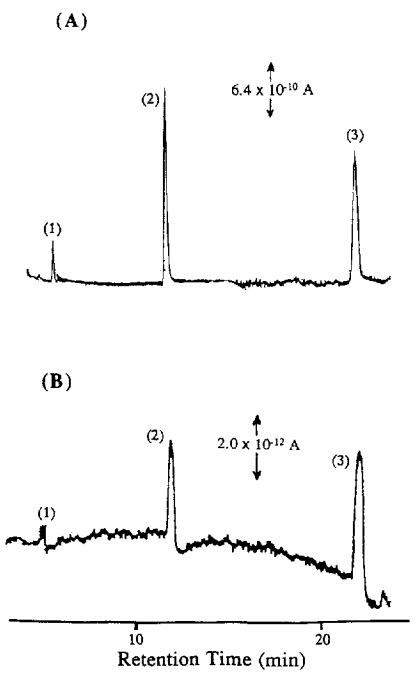

Fig. 2. A comparison between (A), new-SID and (B), conventional SID. In both cases the detected gas chromatograms were of 5 ng benzene (marked as 1), 5 ng toluene (2) and 5 ng m-xylene (3) mixture in acetone solution. This mixture was injected into a gas chromatograph having a 25-m capillary column (FFS ULBON HR1, 0.32 mm I.D.) at 40°C. The upper trace is of new SID detection with $T_n = 930$°C and $T_s = 900$°C, while in the lower trace the conventional SID was operated at $T_s = 800$°C.

3.2.2. Polycyclic aromatic hydrocarbons (PAHs)

In Fig. 4 a new-SID chromatogram of a series of polycyclic aromatic hydrocarbons is again compared with FID. The difference in the two chromatograms

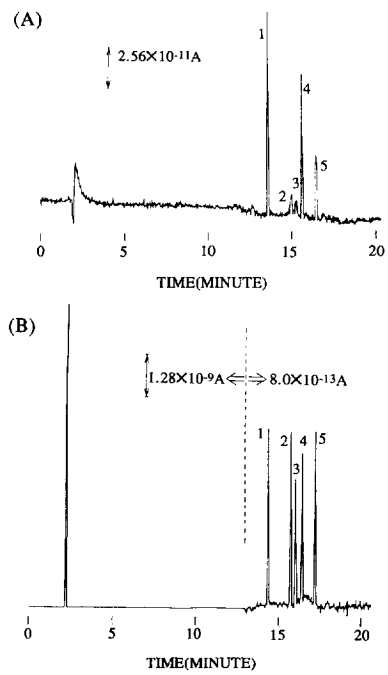

Fig. 3. Analysis of monoterpenes with two different detectors. (A), SID channel and (B), FID channel. A new SID detection with $T_n = 680$°C and $T_s = 700$°C was made. Sample: each peak corresponds to 0.5 ng of the substance. Peaks: 1 = α-pinene; 2 = β-pinene; 3 = myrcene; 4 = 2-carene and 5 = (+)-limonene.

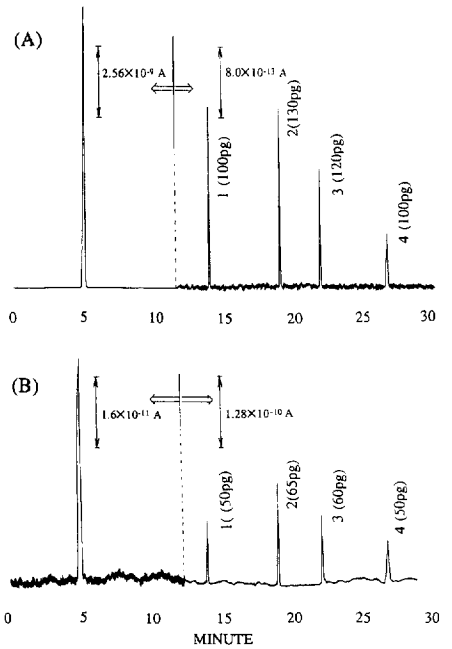

Fig. 4. A comparison between (A), conventional FID (upper trace) and (B), new-SID (lower trace). In both cases the detected gas chromatograms were of a mixture of polycyclic aromatic hydrocarbons: 1 = naphthalene, 2 = anthracene, 3 = pyrene and 4 = chrysene mixture in benzene solution. The different sample sizes were used in the FID and new SID injections, as indicated. The upper trace is of new SID with $T_n = 930°C$ and $T_s = 900°C$, while in the lower trace the FID signal is given. The FID conditions are: H_2 flow-rate, 30 ml/min; air flow-rate, 600 ml/min.

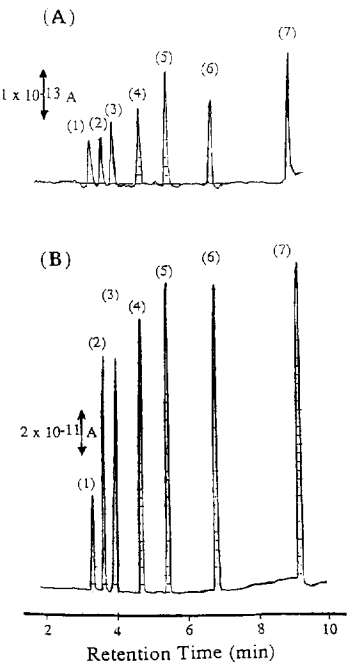

Fig. 5. A comparison between (A), conventional FID (upper trace) and (B), new-SID (lower trace). Both gas chromatograms are of a mixture of 5 ng alkyl alcohols $C_nH_{2n+1}OH$ ($n = 1–5$); 1 = methanol, 2 = ethanol, 3 = isopropanol, 4 = *n*-propanol, 5 = 2-butanol, 6 = 1-butanol and 7 = *n*-pentanol. The new-SID conditions are; $T_n = 930°C$, $T_s = 900°C$. GC conditions as in Fig. 4.

is clear. In the case of pyrene, the detection capability of the SID is 8.9 times higher than that obtained with the FID.

3.2.3. Alkyl alcohols

Fig. 5 shows examples of responses obtained when a mixture of alkyl alcohols is chromatographed and measured by new-SID and FID. The upper trace shows these compounds analyzed by FID at an electrometer setting of 10^{-12} AFS. The measurements in both the SID and FID modes were made under the optimum conditions for MDA. The optimum conditions for FID gave the sensitivity at 0.009 C/s for *n*-propane, which is very close to the literature values [9]. The lower trace shows the same sample analyzed by the new SID at a setting of $2 \cdot 10^{-10}$ AFS. It was necessary to attenuate 200 times to keep the response on scale for all the sample components whose size is $5 \cdot 10^{-9}$ g each.

By comparing the records of Figs. 4 and 5 from both detectors, it is found that (1) SID provides significantly higher sensitivity than FID, while the noise level for the former is about two orders of magnitude higher than the latter, (2) the new-SID sensitivity somehow depends on the molecular (or alkyl chain) mass, and (3) the SID detector provides as good resolution as FID, demonstrating that the new detector responds rapidly enough to follow sharp capillary peaks. This is consistent with the fact that (1) the surface ionization response time is short, because of its character due to scattering events and (2) the use of low-pressure or vacuum outlet techniques for GC is widely improved with greater separation efficiency [10].

On occasion, the baseline also exhibits a sharp backward response at the peak tail. No completely satisfactory explanation of this unstable baseline has

been formulated as yet. Attempts to find the cause were not successful. The similar SID response appears sensitive to the analyte matrix, which could be a difficult problem to solve and could result in poor quantitative analysis.

4. Conclusion

We have developed analytical schemes involving sensitive detection using a novel SID method which incorporates a supersonic free jet. The new-SID acts as a universal detection method with additional selectivity toward some species that have low IE.

In its present state of development, the response of the hyperthermal-SID to most organic compounds, including aliphatic alcohols, is about 100 times greater than the response obtained from the same compounds with conventional FID. The detector has a minimum detectability of 10^{-12} g/s of toluene, a selectivity relative to hydrocarbons of ≥ 10, and a linear range of operation of 10^4.

Experiments are planned for the continuation of this work, focusing on the improvement of nitrogen–phosphorus detection (NPD) (or thermionic ionization detection) which works on the principle of negative surface ionization [11].

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