

Miniaturized mass-selective detector with atmospheric pressure chemical ionization

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Abstract

The miniaturized mass-spectrometric detector with atmospheric pressure chemical ionization (APCI) is described. The analyzer employed in this instrument is the monopole with rod 54 mm in length and 2 mm in radius, which retains its efficiency up to 0.13 Pa ($\approx 10^{-3}$ Torr). Together with the ion source, channeltron ion detector, radio frequency power supply and preamplifier, it is packed into a case with dimension of 185 mm \times 100 mm \times 70 mm. Mass spectrometer with the whole vacuum system weighs about 20 kg. In spite of low power of the vacuum system, the limit of detection at ppt level is achieved. The “strong” fragmentation mode is suggested for high-specific detection of phosphor-containing substances. The detector conforms to multicapillary column attachment.

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1. Introduction

One of the actual trends of the development of mass-spectrometric instrumentation is building field device for harsh environments. Here, the most important characteristics are reliability, endurance, small size, low cost and low power requirements. A number of advances in this field, as well as the major trends, are discussed in reviews [1,2]. In the previous review [3], the characteristics of miniature mass analyzers were discussed. The important fact is that by reducing the size of mass analyzer the size of the vacuum system and power supplies can also be reduced.

Small size mass spectrometers described in literature make use of electron impact (EI) ionization. The increasingly popular mild ionization techniques, which are performed at/or near atmospheric pressure, i.e., atmospheric pressure chemical ionization (APCI), have several advantages compared to low pressure EI ionization technique. A summary of this developments was presented in the previous paper [4].

This paper presents the miniature mass-spectrometric detector with APCI, which consists of miniature monopole mass analyzer with power supplies, detachable APCI ion source and compact vacuum system. Inlet part is designed for flow rate 1 ml/s, which agrees with optimal flow for multicapillary column, which can be immediately connected to mass spectrometer. The limit of detection at ppt level is demonstrated.

2. Experimental

2.1. APCI ion source design

Classic design of APCI interface was used with a two-stage differentially pumped system consisting of declustering region pumped by a rotary pump and a mass analyzer region pumped by a high vacuum pump [5]. The pumping speed of rotary pump is 0.1 l/s (NVR-0.1D, Vakma, Kazan, Russia). The pumping speed of turbo pump is 40 l/s (NVT-40, Prizma, Iskitim, Russia). The sampling nozzle orifice diameter is 80 μ m, which gives pressure of about 1.3×10^3 Pa (≈ 10 Torr) in first vacuum region. The skimmer orifice diameter is 100 μ m. The distance between them

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is 3 mm. An electric field is applied in first vacuum region to achieve collision-induced dissociation of the ions. The ions generated by corona discharge with stabilized current which can vary at the range 10^{-2} to $10 \mu\text{A}$. The distance between corona needle and sample orifice is 1.8 mm. To avoid “memories” effect, the region of ionization is heated to 110°C . The flow rate of carrier gas through ion source determined by first diaphragm diameter is $1 \text{ cm}^3/\text{s}$. For sample introduction heated (120°C) Teflon line is attached to ion source.

2.2. Mass spectrometer design

The mass analyzer is a monopole mass filter with a rod 54 mm in length and 2 mm in radius, which retains its efficiency up to 0.13 Pa ($\approx 10^{-3} \text{ Torr}$). Layout of mass analyzer is shown in Fig. 1. Together with the ion source, channeltron ion detector VEU-6 (Gran, Vladikavkaz, Russia), RF power supply and preamplifier, it fits in a space $185 \text{ mm} \times 100 \text{ mm} \times 70 \text{ mm}$ dimensions.

Under standard conditions (accelerating voltage 20 V; $U/V = 0.12$; frequency 5 MHz), the mass spectral peaks show a width at half height of about one unit of m/z at the range from 12 to $200 m/z$. The mass range may be extended by reducing U/V ratio with slight deterioration of resolution. The mass spectrum of diisopropyl methylphosphonate (DIMP) is shown in Fig. 2, the unit resolution is demonstrated.

Mass spectrometer with the whole vacuum system and control unit is shown in Fig. 3. The total weight of device is less than 20 kg. It is significant, that when the carrier gas is air rather than helium, the rotor speed of turbo pump can be reduced, thus increasing shock resistance and decreasing power requirements.

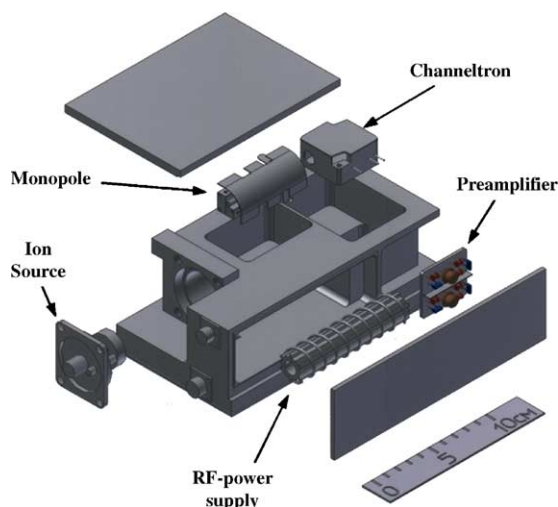


Fig. 1. Layout of mass analyzer.

2.3. Sample preparation

To generate standard vapor concentrations for evaluating mass spectrometer performances, permeation tubes and diffusion tubes were used as vapor sources.

The sources of dimethyl methylphosphonate (DMMP) and diisopropyl methylphosphonate were permeation tubes (KIN-TEK, La Marque, TX).

To generate the vapours of pyridine and aromatic hydrocarbons diffusion vials were used. A diffusion vial consists of glass vessel with substance and stainless steel capillary. The two types of capillary were used: $130 \text{ mm} \times 0.35 \text{ mm}$ and $130 \text{ mm} \times 0.75 \text{ mm}$.

To generate the vapours of tributyl phosphate (TBP) diffusion vials (VICI Metronics Inc., Santa Clara, CA) were used.

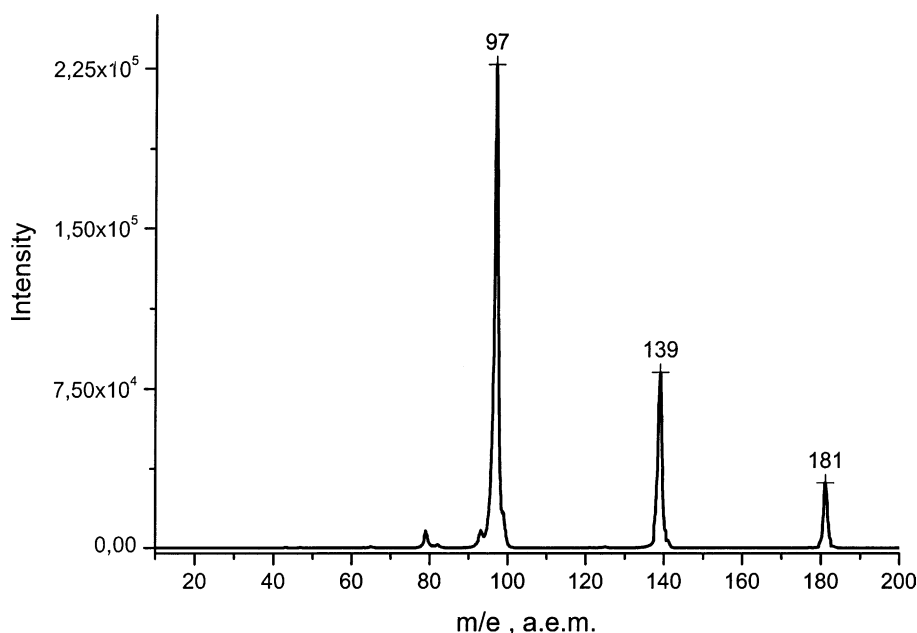


Fig. 2. The mass spectrum of diisopropyl methylphosphonate (declustering voltage 60 V).

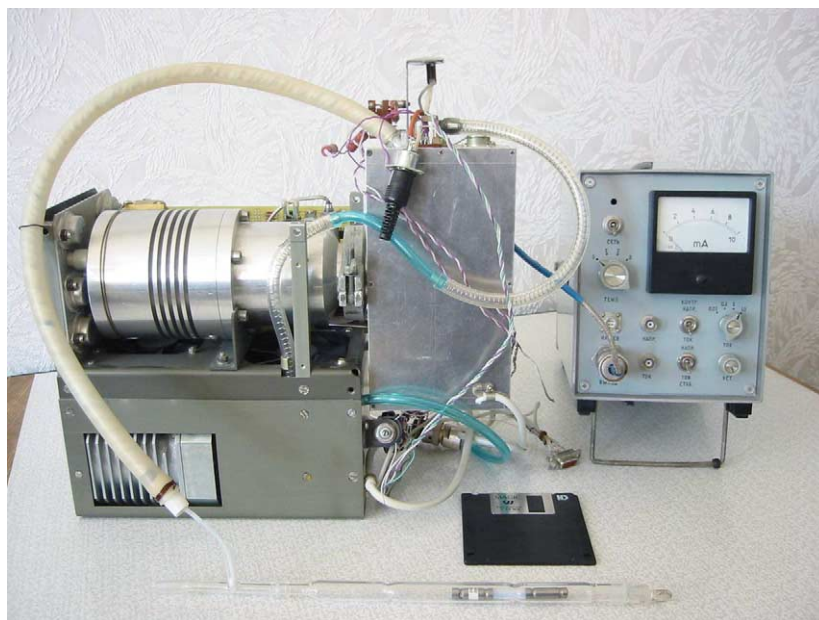


Fig. 3. Miniaturized mass-selective detector with atmospheric pressure chemical ionization: the mass analyzer with the whole vacuum system (on the left) and control unit (on the right).

Geometrical size of diffusion tube ($7.62 \text{ cm} \times 0.00196 \text{ cm}$) gives rate of diffusion 10 ng/min at 365 K .

To vary concentrations the dilution flow changes from 0.1 to 4 l/min . The carrier gas was the laboratory air passed through charcoal filter and silica gel dryer. To vary humidity wet air was added. Humidity was controlled by sensor IH-3610-2 (Honeywell Inc., El Paso, TX). In the experiment, the humidity was kept at 10% .

3. Result and discussion

It is generally known [4] that sensitivity of APCI mass spectrometer system is determined by the throughput of gas into the analyzer or, in other words, the pumping speed of vacuum system. In our case, for the goal of reducing the size of the system, compact pumps were used. The inlet flow rate of gas in our detector is at least 50 times lower

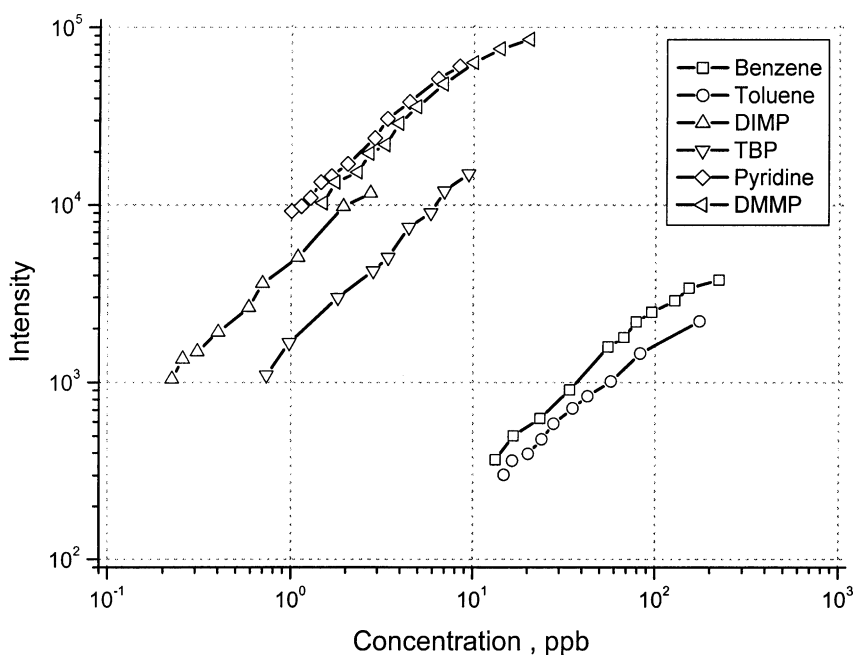


Fig. 4. The dependencies of response on concentration for a number of compounds. DIMP: diisopropyl methylphosphonate; TBP: tributyl phosphate; DMMP: dimethyl methylphosphonate.

than that of various API sources described in scientific literature [6]. At the same time, thanks to the miniaturization and to minimization of ion losses at transmission into vacuum, we managed to retain high sensitivity, inherent in APCI technique. The dependencies of response on concentration for several classes of substances are shown in Fig. 4. Apparently, for high basicity substances, such as amines and phosphorus-containing substances, the limit of detection is in low ppt region. At the same time, for aromatic hydrocarbons it is low ppb region.

As it is inherent in APCI technique, a collision-induced dissociation occurs in first vacuum region. The degree of primary ions fragmentation is controlled by electric field strength in this region. The typical structure of fragmentation for phosphor-containing substances is illustrated in Fig. 5 by the example of DIMP. Thanks to the short distance between the electrodes, we managed to reach “strong” dissociation with formation of elementary fragments. For DMMP, DIMP and TBP those fragments are PO_2^+ and PO^+ and even P^+ (with 63, 47, 31 m/z , accordingly). In such harsh conditions,

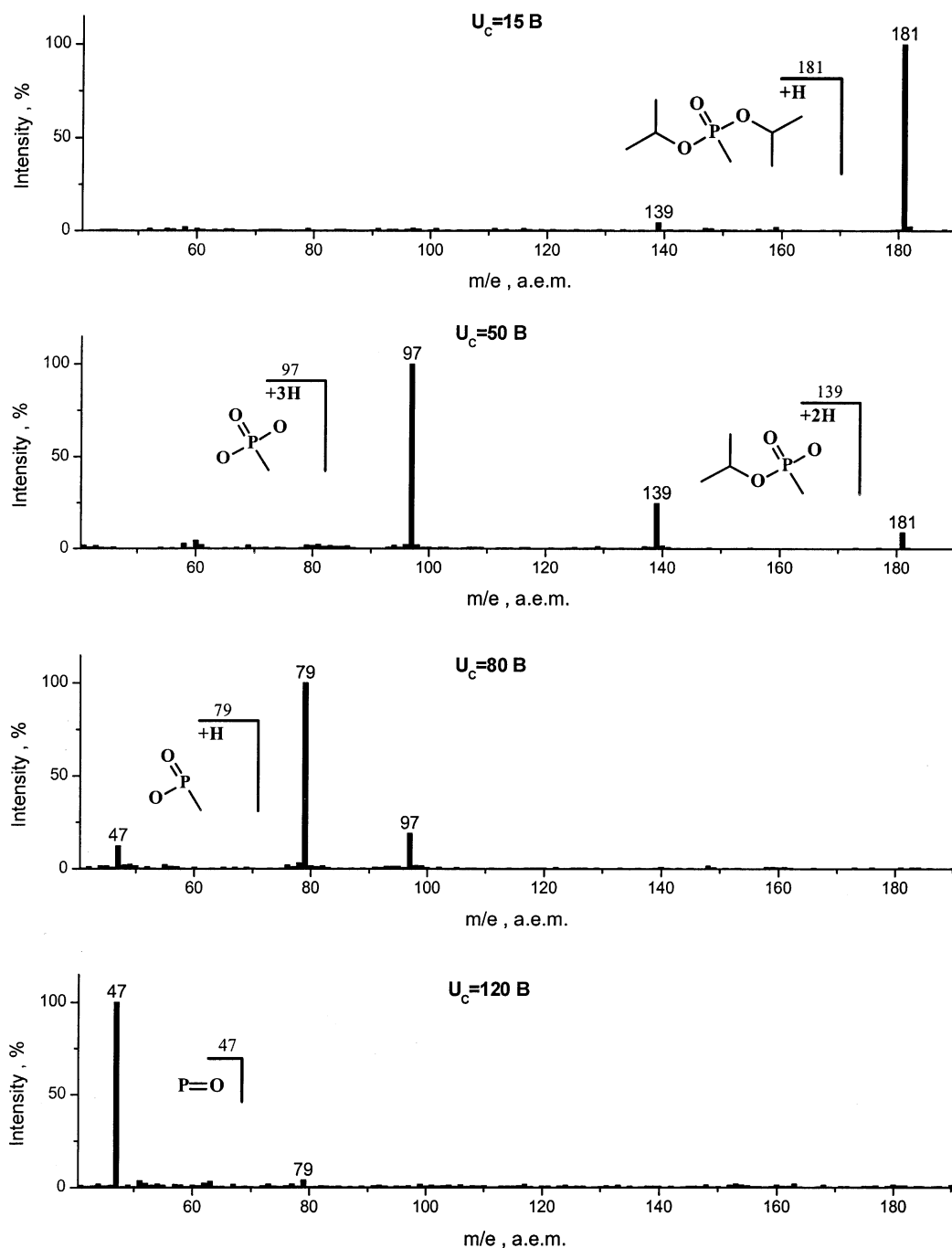


Fig. 5. The structure of fragmentation for diisopropyl methylphosphonate.

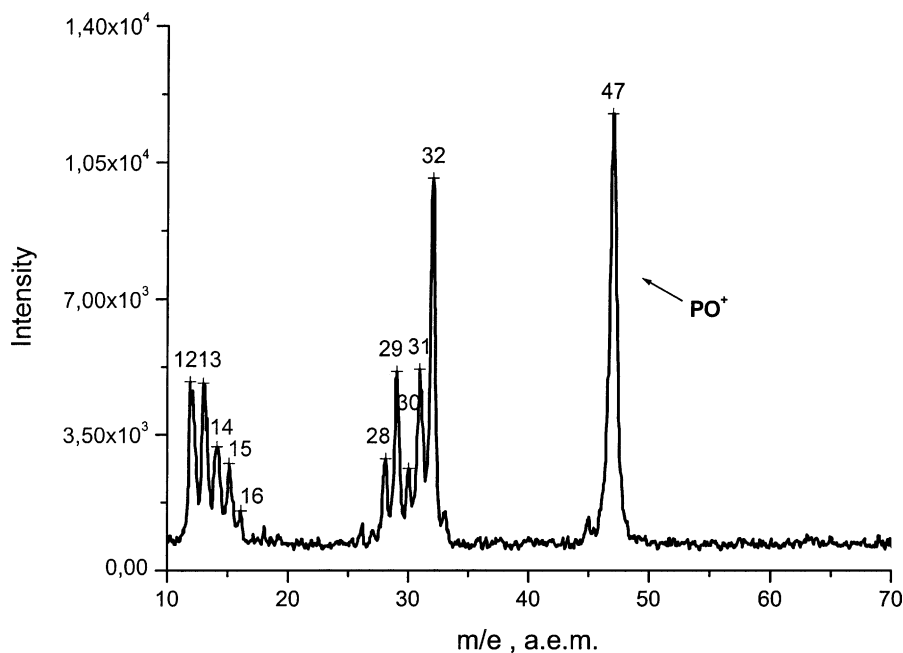


Fig. 6. Mass spectrum of diisopropyl methylphosphonate at high declustering voltage (210 V).

other substances (for example, background carbohydrates) produce fragments at the range 12–32 m/z . Such mass spectrum of DIMP at declustering voltage 210 V is shown in Fig. 6. This mode may give good result for high-specific detection of phosphor-containing substances.

The inlet of the mass spectrometer can accommodate a gas flow rate of 1 ml/s, which matches the optimal flow rate for the multicapillary GC columns through which sample gas enters the mass spectrometer. In that case, the flow of buffer gas through the column (1 ml/s) is provided by the natural pressure difference between the inlet of the GC column and the inlet of the first stage of vacuum system. Multicapillary columns will provide several advantages in comparison with other types of GC columns including:

- high volume flow for increased sensitivity;
- high separation factors at high flow velocities of carrier gas;
- high column capacity (column does not alter its properties with high impurity levels in sample gas);
- multicapillary column needs lower operational temperature, and thus lower power consumption.

It is expected that 20–30 s will be enough to get necessary degree of GC separation. The results of junction miniaturized APCI detector with multicapillary column will be published in near future.

4. Conclusion

The miniaturized mass-spectrometric detector with atmospheric pressure chemical ionization is described. The analyzer employed in this instrument is the monopole with rod 54 mm in length and 2 mm in radius, which retains its efficiency up to 0.13 Pa ($\approx 10^{-3}$ Torr). Together with the ion source, channeltron ion detector, radio frequency power supply and preamplifier, it is packed into a case with dimension of 185 mm \times 100 mm \times 70 mm. Mass spectrometer with the whole vacuum system weighs about 20 kg. In spite of low power of the vacuum system, the limit of detection at ppt level is achieved. The “strong” fragmentation mode is suggested for high-specific detection of phosphor-containing substances. The detector conforms to multicapillary column attachment.

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