

Field gas chromatography–mass spectrometry for fast analysis

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Abstract

The objective of this presentation is to demonstrate the original device and procedure for fast gas chromatography–mass spectrometry (GC–MS) analysis of gaseous and liquid samples and to discuss its features and capabilities. The concept was developed in order to expand the range of compounds suitable for GC separation and to reduce the time of analysis. Field GC–MS, consisting of original “concentrator–thermodesorber” (CTD) unit, multiple module GC system and compact magnetic mass spectrometer with powerful two-stage vacuum system and multicollector ion detector, is represented. The whole weight of the device is 90 kg. Power consumption is 250 W. The device and analytical procedures allow high speed screening of toxic substances in air and extracts within 100 s per sample. The examples of applications are described, including fast screening of tributyl phosphate (TBP) in air at low ppt level at the rate 1 sample/min.

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Keywords: Field analysis; Real-time analysis; Portable instrumentation

1. Introduction

One of the most active trends in the area of analytical instrumentation is the development of field-portable devices directed on fast in site analysis. Most of the laboratory-based methods are available now in the field.

The combination of gas chromatography with mass spectrometry (GC–MS) represents one of the most reliable methods for the analysis of complex mixture of organic compounds. Field-portable GC–MS system and application have also evolved considerably over the past decade. The analytical advantages of rapid response time combined with high detection efficiency, accuracy and data quality have helped this expansion. Several commercial field-portable GC–MS systems are well-known, including MM1 [1] and EM640 [2] by Bruker, SpectraTrack [3] by Viking Instruments.

Trends and advances in portable analytical instrumentation were discussed in previous reviews [4,5]. Two important trends were highlighted: the capability to detect specific compounds in complex mixture in a matter of seconds, and the expansion of the volatility range of analytes. Multiple

integrated GC modules were discussed to provide analyses of compounds with widely different chemical characteristics. The role of the integration of sampling and analysis capability is also emphasized.

Thus, given the level of modern technical development, in order to achieve the required limit of detection and specificity, trace level detection systems should be equipped with devices for preconcentration and preliminary separation of sample. Moreover, this increases the duration of the cycle of analysis.

This has a set of reasons. Firstly, known inlet systems with preconcentration and thermodesorption employ additional “focusing” stage (which is necessary for lessening the initial width of the sample plug). Normally, the stage takes a few minutes. Secondly, GC separation takes time. It should also be taken into consideration that in case temperature programming mode is employed before the beginning of the next analysis it is important to cool GC oven to initial temperature (which usually takes a few minutes).

The basic problem which was posed in the process of the development was to provide the limit of detection at ppt level and at the same time the high rate of analysis (up to several analyses a minute).

The objective of this paper is to present the original device and procedure for fast GC–MS analysis and to discuss its features and capabilities. The multiple integrated GC module

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concepts are incorporated into field GC–MS system for the first time.

2. Experimental

2.1. The concept

The “key” elements to solve the problem are the original “concentrator–thermodesorber” (CTD) [6], the multiple GC module “transfer-line” GC system and the compact magnetic double-focusing mass spectrometer with powerful two-stage vacuum system and multicollector ion detector. The appearance of the device is shown in Fig. 1.

CTD is a very important feature of the overall system, it operates at ambient pressure and has very simple design. It greatly increases the system sensitivity. CTD comprises a thin-walled metal tube with a layer of selective absorbent that traps analyte species from ambient air passing through the tube. Rapid “ballistic” heating then desorbs the trapped species in less than a second, so that any thermal decomposition of fragile species is minimized, which is an important factor in the case of chemical weapons agents (CWAs) or other unstable substances. The particular feature of this device is that during the desorption the sample immediately enters the GC column as narrow plug, usually its width is less than 1 s. As soon as the “flash” heating has desorbed the trapped species, the concentrator is entirely purified and is ready for the next analysis. The whole procedure takes only a few seconds.

The multiple GC module system contains several different GC “transfer-line” channels. Every channel has its own small oven and direct inlet in MS ion source. The principal mode of separation is isothermal. The main peculiarity of such GC system is the opportunity to analyze substances which differ greatly in boiling temperature within a single short GC run without programming the temperature.

The GC–MS device is based on the compact double-focusing stationary magnetic type mass spectrometer with the

original multicollector ion registration system. The compact rugged vacuum system allows the total flow of helium to be up to 8 ml/min. It is due to the high productivity of the vacuum system that the simultaneous attachment of multiple GC modules is made possible.

2.2. CTD and GC system design

The major components of CTD are fast-detached concentrator, which constitutes a thin-walled metal tube with layer of sorbent, and thermodesorber designed for the ballistic heating of concentrator.

The concentrator is a stainless steel tube with wall thickness 0.15 mm, i.d. 2.2 mm and length 120 mm. Inside, there is a sorbent layer Tenax TA or Thermo-trap TA gripped with silanized glass wool taps and metal gauze on both sides. The length of sorbent layer is 5 mm, volume $1.9 \times 10^{-2} \text{ cm}^3$, weight 5 mg. The length of wool layer is 1 mm. The distance from sorbent to the edge of tube is 10 mm.

Vapours and aerosol particles are sampled by means of pumping air through concentrator. Organic substances from volatile solvent are sampled by means of placing aliquot of solution into concentrator, with subsequent removal of solvent from sorbent by means of the aspiration of carrier gas through concentrator.

The scheme of CTD with GC system is illustrated in Fig. 2.

Thermodesorber is a thick-walled metal tube, with one open edge. To the other edge a GC column (or several columns) is attached. Through the orifice in the wall of the thermodesorber channel the curtain flow of carrier gas is conducted. Mainly, helium is used as carrier gas. Part of this flow is entrained into the GC column(s), while the other part is propelled into the atmosphere through the open edge of thermodesorber. The continuous venting of thermodesorber prevents air and dust from entering the GC column(s). The inlet system is equipped with flexible tube to deliver carrier gas into the concentrator.



Fig. 1. Field GC–MS for fast analysis.

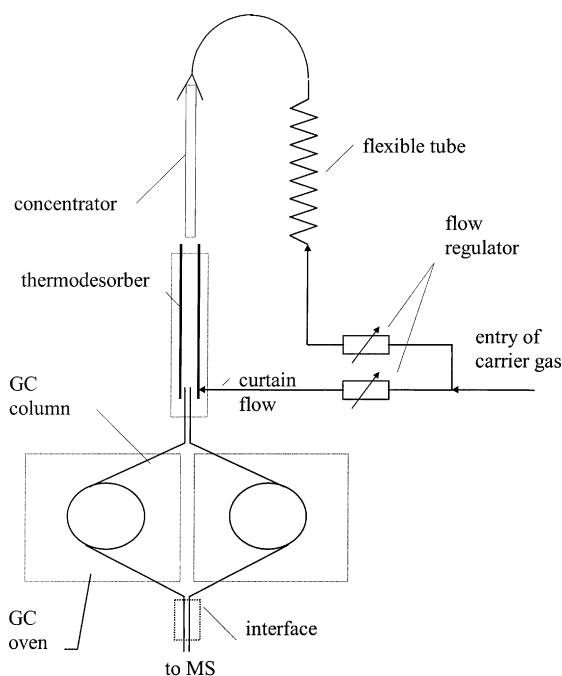


Fig. 2. Schematic diagram of concentrator–thermodesorber and multi-channel GC system.

To enter the sample, the concentrator is made hermetically attached to the flexible tube and is fast entered into the thermodesorber, which is kept at the temperature about 300 °C. At ballistic heating of the concentrator, sample placed in it turns into gas phase and with the carrier gas is directed to the GC column.

The diagram which illustrates the injection procedure in more detail is shown in Fig. 3.

At standby mode, the curtain flow of carrier gas is delivered into the lower part of the thermodesorber. The flow blows round the entry of the column. The flow Q_1 through the column is formed by the drop pressure between the entry and the exit of the column, while the quantity Q_1 is defined by gas resistance of the column. In regular conditions, it equals 1–3 ml/min for each column. Part of the curtain flow of carrier gas is intercepted by the column, while the other part vents the thermodesorber and keeps air from entering the column.

At injection mode, the concentrator is attached to the flexible tube with carrier gas and is introduced into thermodesorber. In this case, the sorbent layer in the concentrator appears close in front of the entry of the column. As the concentrator is being heated, volatile substances are desorbed and with carrier gas enter into the column. Because of the low heat capacity of the concentrator, heating and desorption take place within a fraction of a second.

After introducing the sample, the concentrator is withdrawn out of the thermodesorber. Carrier gas from the curtain flow is delivered into the column. In this mode GC separation takes place.

The suggested principle of operation and the design of the inlet system allows to form the initial sample plug narrow enough, without additional focusing stage. The whole procedure of sample injection takes a few seconds and thus allows to use this device for very fast analysis. In addition, the sample is carried into the GC column without any contacts with the construction parts and without any losses. The residence time for sample substances at high temperature is a fraction of second. This is very important for analysis of CWAs and other thermolabile and reactive substances.

At the instant the sample is introduced, the concentrator is entirely purified and is ready for the next analysis. Thanks

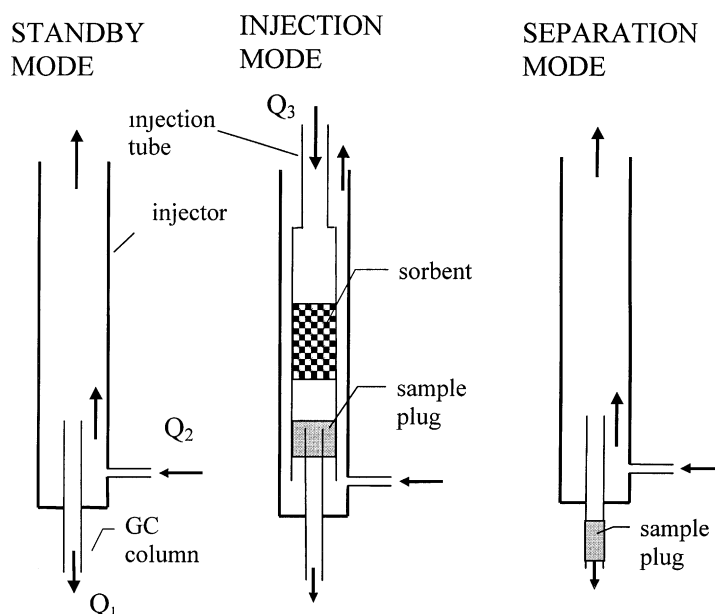


Fig. 3. Schematic diagram of concentrator–thermodesorber operation.

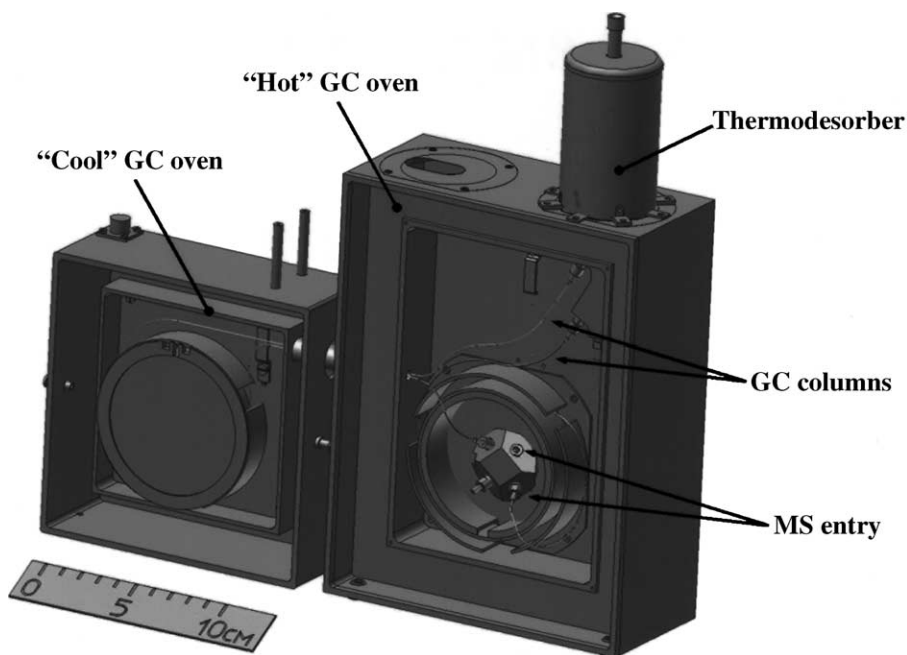


Fig. 4. The layout of GC system.

to that, there is absolutely no such problem as residual effects.

The multiple GC module system contains several different GC “transfer-line” channels. Every column is attached to the thermodesorber and has direct inlet in MS ion source. Usually, 5–10 m length columns are used.

The layout of the inlet system is illustrated in Fig. 4. It has two GC ovens and a thermodesorber. Up to four GC columns at a time can be attached to the inlet system and ion source. An additional inlet unit may be installed.

2.3. Mass spectrometer

For high speed GC separation, high spectral scan rate will be required. A quadrupole mass spectrometer most commonly used with GC may be scanned at the rate of 0.1 s per decade, but at the expense of sensitivity. In some cases, the sensitivity of such scanning mass spectrometer can be enhanced by the technique of selected ion monitoring (SIM). SIM, however, has limited application for the unambiguous identification of compounds in complex mixtures. The non-scanning mass spectrograph suited for the measurement of narrow GC peaks with an electro-optical ion detector (EOID) was described in the previous paper [7]. The same Mattauch–Herzog type mass analyzer is exploited in our instrument. The difference is the usage of multicollector ion detector [8] instead of EOID, and the powerful two-stage vacuum system allowing the total flow of helium to be up to 8 ml/min. The block diagram of the functional components of the whole GC–MS system including the mass spectrometer is shown in Fig. 5.

Because of the big angular aperture, secondary ions and molecules with high energy produced in the recharging pro-

cess result in the increase of the background ion current of EOID and reduction of linear dynamic range. EOID also has limitation in resolving power. The multicollector ion detector has no such problems.

The multicollector ion detector consists of five collectors located in the focal plane of the magnet. The collector consists of channeltron (VEU-6, Gran, Vladikavkaz), diaphragm with slit 100 μm and additional diaphragm for restriction of angular aperture.

The registration of mass spectrum is carried out by means of alteration of ion energy at simultaneous measurement of the ion current in each collector. At that, the total mass spectrum will be the superposition of mass spectra registered by each collector. Combining all the collectors and control electronic with automated system of data acquisition provides virtually simultaneous registration of ions by all the collectors, fast processing mass spectrometric data, and storage of large amount of total mass spectra.

The vacuum system consists of two rugged turbomolecular pumps with pumping speed 100 l/s (NVT-100, Prizma, Iskitim), compact rough pump with pumping speed 0.1 l/s (NVR-0.1D, Vakma, Kazan). The regions of ion source and mass analyzer are separated by slit (0.1 \times 5 mm) and are pumped out separately. The pressure at those regions is 0.13 Pa ($\approx 10^{-3}$ Torr) and 1.3×10^{-3} Pa ($\approx 10^{-5}$ Torr).

Mass analyzer parameters: electron impact ion source operating at 70 eV, cylindrical electrostatic condenser with mean radius 80 mm, turning angle 40°, focal length 37 mm, magnetic sector material SmCo, a magnetic induction in the gap between the pole pieces of permanent magnet 0.6 T, turning angle in magnetic field 80°, maximum radius of ion trajectory 172 mm, mass ranges 12–400 (12–600) Da

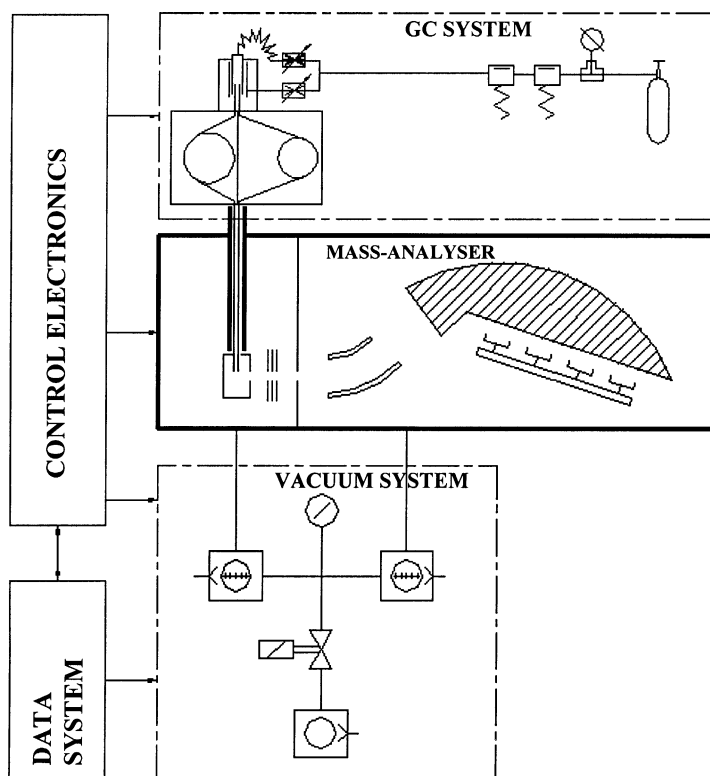


Fig. 5. The block diagram of the functional components of the field GC-MS.

is covered under the accelerating voltage altering from 3600 to 1800 (900) V, and resolution is 600 on 50% level.

The data system processes and stores the measured data. The mass spectra match well with those of commercial databases and the identification of unexpected compounds can often be done by comparison with the NIST/EPA/NIH mass spectra database, with the help of Automated Mass Spectral Deconvolution & Identification System (AMDIS) by National Institute of Standards and Technology [9].

The weight of the whole GC-MS device, including the vacuum system, the high-pressure gas cylinder with helium and the data system, is 90 kg. Power consumption is 250 W.

2.4. Materials

To generate the vapours of tributyl phosphate (TBP) diffusion vials (VICI Metronics Inc., Santa Clara, CA) were used. Geometrical size of a diffusion tube (7.62 cm × 0.00196 cm) and $T = 365$ K gives the rate of diffusion 10 ng/min. To vary concentrations the dilution flow changes from 0.1 to 4 l/min. The gas for dilution flow was the laboratory air.

The materials for the concentrator: glass wool, DMCS treated; Tenax TA (35–60 mesh); Thermo-trap TA (60–80 mesh) (Chrompack, The Netherlands). For the injection of

extracts VARI pipette AW-20 (High Tech Lab, Warsaw, Poland) was used.

3. Results and discussion

The advantages of the described inlet and separation system are illustrated in the Fig. 6 which demonstrates the GS/MS run for the mixture of four real chemical agents: sarin (isopropyl methylphosphonofluoridate), soman (pinacolyl methylphosphonofluoridate), mustard (bis (2-chloroethyl)sulphide) and VX (*O*-ethyl-*S*-2di-isopropylaminoethyl methylphosphonothiolate) in hexane with concentration 10^{-3} mg/ml in the presence of impurities. GC conditions are shown in the figure.

To perform the analysis, 10 μ l of solution was injected into the concentrator containing sorbent Thermo-trap TA by an automatic pipette. Next, hexane was removed from sorbent at the temperature 50 °C by the pumping of carrier gas during 30 s at 30 cm³/min. This sample was analyzed with full mass spectra registration.

In this case, thanks to parallel GC channels, at the same time we can detect sarin with boiling temperature 150 °C and VX with boiling temperature 300 °C. In this mode the whole analysis takes approximately 100 s. Since isothermal mode of separation is used, GC-MS is ready for the next analysis right after the elution of mustard, and thus approximately 30 analyses/h can be performed.

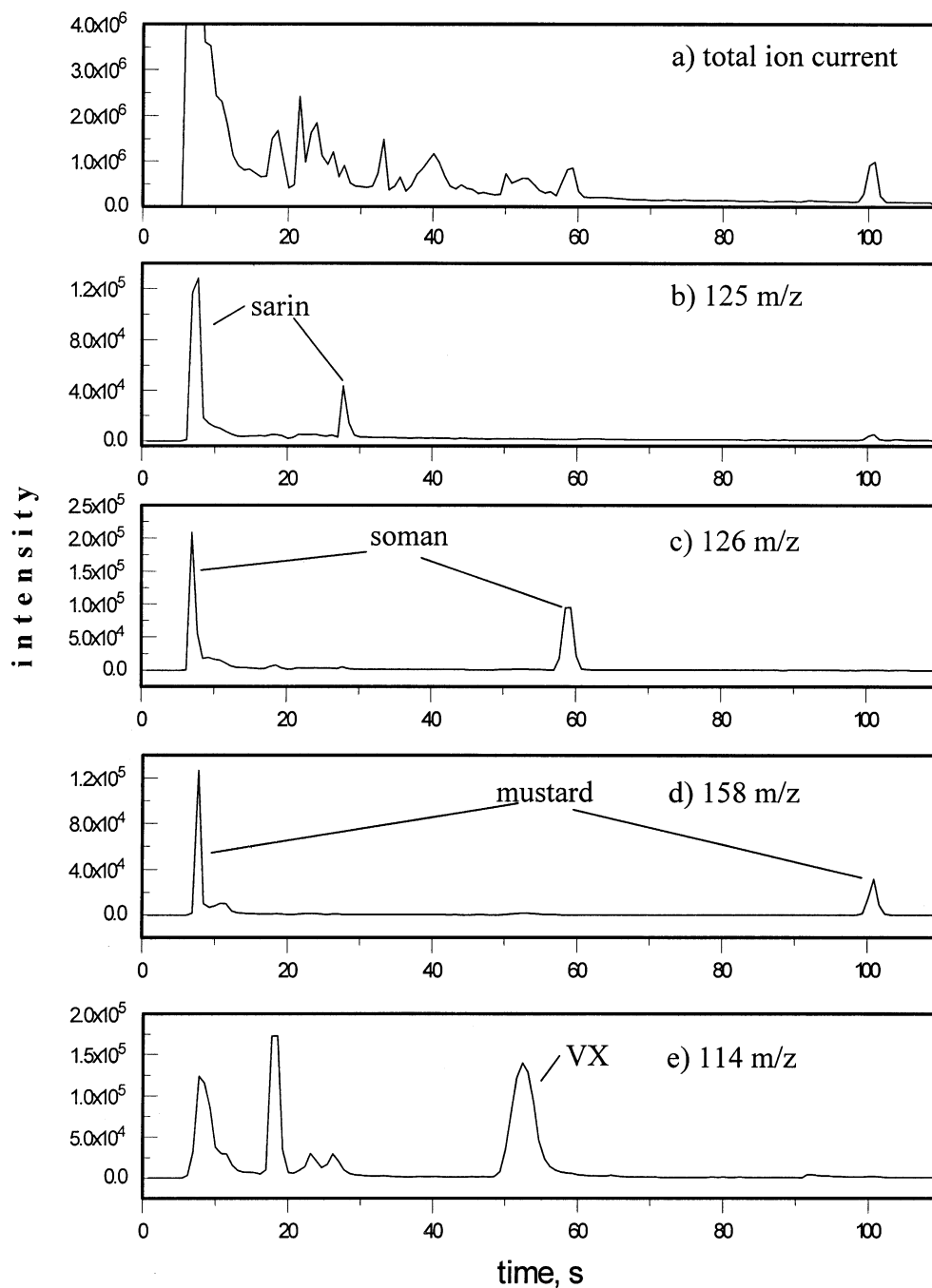


Fig. 6. High speed GC–MS run of CWAs mixture, using two-channel GC system. (a) Total ion current chromatogram; (b–e) mass-selected chromatograms. The data are extracted from full scan spectra (47–280 m/z). The configuration of GC system. first column: HP-1, 5 m \times 0.25 mm; 0.25 μ m, $T = 150^\circ\text{C}$; second column: HP-1, 10 m \times 0.25 mm; 0.25 μ m, $T = 90^\circ\text{C}$; temperature of thermodesorber 300°C .

Such procedure of preparing the samples with large volume injection (10 μ l) provides to avoid any steps of enrichment in extract and allows to replace microsyringe by micropipette with disposable tips. That provides the decreasing of labour intensiveness and time consuming of the analysis. On the other hand, the probability of sample contamination is decreasing.

Another example of the high productivity of the device is shown in Fig. 7. Ion profiles of 155 m/z fragment ion of TBP are presented during repetitive sample injection. The concentration of TBP 5×10^{-7} mg/l (45 ppt) was generated in air as described in part 2.4. Fifty millilitres of air was drawn through the concentrator by gas syringe within a time of 20 s. Then analysis in single ion monitoring (SIM) mode

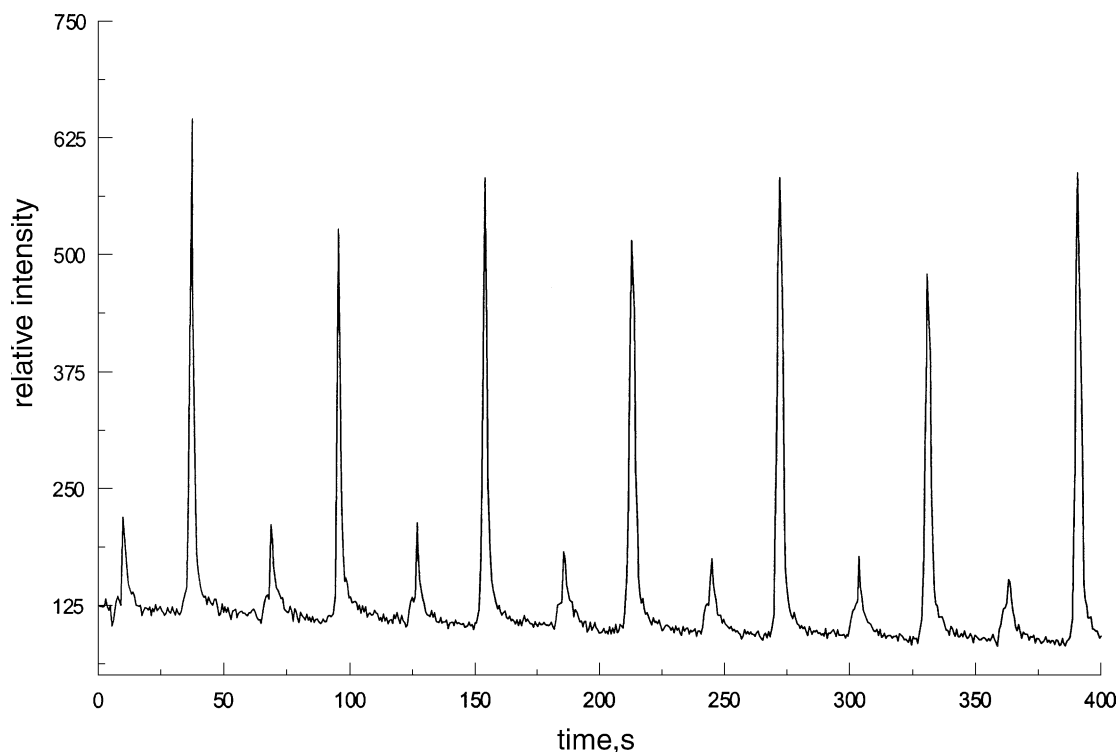


Fig. 7. Fast GC–MS screening run for tributyl phosphate (TBP) in air (mass-selected chromatogram of multiple injection of sample by 155 m/z ion fragment). Concentration of TBP is 5×10^{-7} mg/l (45 ppt). The rate of analysis is approximately 1 analysis/min. GC conditions: column DB-1, 5 m \times 0.25 mm; 0.25 μ m, $T = 150^\circ\text{C}$.

was produced. For achieving the maximal rate of analysis two concentrators were used in turn. In this way, the rate more than 1 analysis/min is achievable. The GC conditions are shown in the figure.

4. Conclusion

Field GC–MS, consisting of the original “concentrator–thermodesorber” unit, multiple module GC system and compact magnetic mass-spectrometer with powerful two-stage vacuum system and multicollector ion detector, is represented.

The combination of engineering solution provides the high rate of analysis at high sensitivity and high reliability. The device and analytical procedures demonstrate high speed screening of toxic substances in air and extracts. The advantage of getting immediate on-site analytical results essentially reduces the cost without loss of quality. The example of analytical procedure was shown with the analysis of tributyl phosphate in air at 45 ppt level within 1 min per sample.

The important resources for further evolution of the presented device is the high resolution (up to 1500) of mass analyzer, and increasing of the ion detector number.

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