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Enrichment and mass spectrometric analysis of trace impurity concentrations in gases

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SUMMARY

An apparatus for enrichment of trace impurity components in gases employing mass spectrometry for analysis is described. The main component is a zeolite-packed chromatographic column. The analytical procedure is carried out step by step: first the trace components are trapped on the adsorbent employing the frontal analysis technique, then the pressure in the column is decreased to a high vacuum by cryopumping and finally the adsorbed trace components are desorbed directly into a mass spectrometer for analysis. The analytical efficiency of the method is demonstrated. Detection limits are in the low-ng/l range.

INTRODUCTION

In certain fields of gas analysis (pollution control, semiconductor industry), analytical methods with very low detection limits (ppm, ppb[a]) are necessary. Conventional mass spectrometers are useful devices for trace gas analysis but their dynamic range (10^6) reduces the possibility of detecting concentrations below 1 ppm[1–8]. In many instances the chemical noise, the variety of contaminants and the fragmentation by electron impact lead to mass interferences that may frustate the analysis. To overcome these problems, various methods[9–11] have been used for enrichment of volatile trace components in gaseous matrices. Cryogenic, adsorptive[12–17] and permeative[18–22] methods for enrichment of trace components in gases are known.

Permeative enrichment is very selective, but using membrane separators enrichment factors of only 10–1000 can be achieved. Gas chromatography–mass spectrometry (GC–MS) has been used in combination with cryogenic or adsorptive enrichment methods[23–27]. This method allows one to separate or discriminate the matrix. In addition, the trapped trace components are fractionated before entering the mass spectrometer. The disadvantage of this procedure is the long and complicated passage of samples into the mass spectrometer. The samples can be contaminated by foreign

[a] Throughout this article, the American billion (10^9) is meant.

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substances, *e.g.*, from the laboratory atmosphere and from the apparatus itself. Moreover, considerable amounts of the sample are adsorbed and therefore lost.

In this paper, a procedure is described for enriching and sampling volatile trace components in gases to improve their MS analysis. The main advantages of the apparatus used are the minimal dead volume, the minimal leak rate and the prevention of dilution of trapped trace components by purging. All steps of the applied procedure (enrichment of trace components, fractionation of the enriched trace components and sampling into the mass spectrometer) were carried out using the same packed column[28,29].

The basic principles of the presented analytical procedure are (1) adsorptive enrichment of trace components in gases using a packed column employing the frontal analysis technique; (2) decreasing the pressure in the column by cryopumping to allow sample transfer into the ion source kept under high vacuum; and (3) fractional desorption of trace components from the adsorbent and their MS analysis.

EXPERIMENTAL

Apparatus

A prototype of the enrichment apparatus (Fig. 1) was attached to the direct inlet (sample rod) of a mass spectrometer (MAT 212) linked to a PDP-11-based data system (SS 188). The apparatus consists of a zeolite-packed chromatographic column 200 mm × 0.6 mm I.D.; Wolfen-Zeosorb 4A, VEB Laborchemie Apolda, G.D.R.; 0.08 g; particle size 0.1–0.15 mm), which is closable at both sides by valves. The inlet side of the column is connected to a sample reservoir and the other end is connected to a sample lock (via the sample rod) of the ion source housing. The column (Cr–Ni steel) may be heated (resistance heating) to 670 K or cooled to 80 K by means of liquid nitrogen.

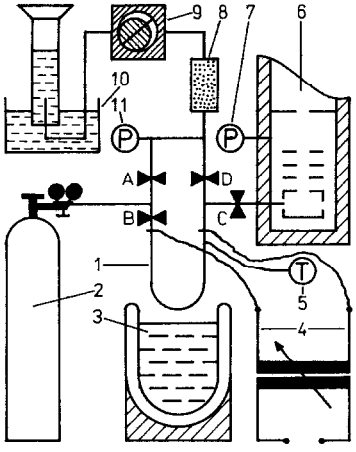

Fig. 1. Schematic diagram of apparatus suitable for the determination of volatile trace components in gases. 1, Packed column; 2, sample reservoir with pressure regulator; 3, cooling bath; 4, adjustable electric heating; 5, thermocouple; 6, mass spectrometer (ion source); 7, high-vacuum pressure control; 8, sorption trap for rotary pump oil vapour; 9, rotary pump; 10, flow meter and chemical trapping of hazardous gases; 11, forevacuum pressure control. A–D, valves.

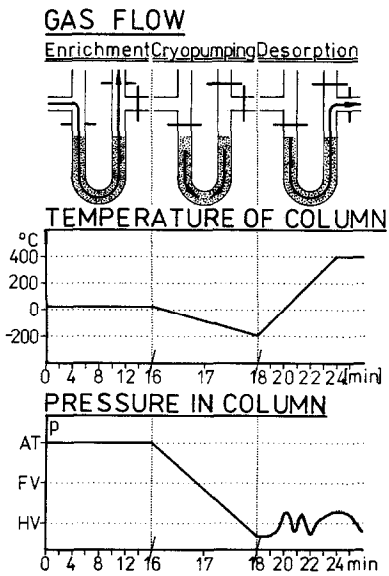

Fig. 2. Schematic diagram of sample line, temperature and pressure in column during enrichment, cryo-pumping and desorption. Enrichment of gaseous impurities in a matrix is carried out at room temperature and atmospheric pressure. Subsequently, the closed column is cryo-pumped, the temperature decreases to 80 K and the column pressure is adjusted to high vacuum. Than the adsorbed impurities are desorbed into the mass spectrometer. During annealing, fractional desorption occurs. For the arrangement of the column (here presented schematically) within the whole system, see Fig. 1.

Procedure

The analytical procedure was carried out in three steps, as shown in Fig. 2. First, volatile trace components in a gaseous matrix to be analysed were enriched in the activated (annealing at 670 K under high-vacuum conditions) zeolite-packed column by adsorption (frontal analysis technique). During the enrichment procedure the sample flows through the column by pumping via the waste line by a rotary oil pump (*cf.*, Fig. 1). The gas flow is adjustable by means of valve B and can be measured. The column temperature depends on the gas matrix to be analysed. The column has to be warm enough to allow the matrix to pass through, but on the other hand it must be cold enough to collect trace components almost completely (*cf.*, Fig. 2). The balance between the gas phase and adsorbed phase leads to the development of a system of adsorption zones.

The pressure in the column roughly equals atmospheric pressure at the end of the enrichment step. To transfer the sample into the ion source of the mass spectrometer, this pressure must be strongly reduced. To achieve this pressure decrease, valve B (*cf.*, Fig. 1) has to be closed at first. Subsequently, the pressure in the column decreases owing to the pumping effect of the rotary oil pump. At this stage it is necesary to take care of losses of adsorbed trace components. Only the matrix component characterized by small interaction forces should principally be pumped off. Therefore, the time required for pumping down has to be very brief. This pressure reduction contributes additionally to the preconcentration of trace components in the column. Subsequently, the whole enrichment step ceases, closing valve D.

The direct coupling of the packed column to the mass spectrometer requires a further pressure reduction in the column. Cryopumping is the most efficient pressure reduction step to allow a sample transfer process without losses. To adjust the pressure to high vacuum, the whole column is cooled to 80 K by immersing it in liquid nitrogen. The movement of impurity zones in the column stops because the gas phase is cryo-adsorbed. Now valve C can be opened without increasing the pressure within the ion source (*cf.*, Fig. 2).

Immediately after opening valve C (*cf.*, Fig. 1), the mass spectrometric analysis must be started. The following parameters have been found to be advantageous: residual gas pressure 10 μPa; maximum pressure during desorption, 1 mPa; temperature of ion source, 370–520 K; optimization of ion source, pressure linear; electron emission current, 0.5 mA; electron energy, 70 eV; investigated mass range 12–200 u; resolution (5% valley): 200–1000 m/Δm; scanning rate, 5–10 s per decade; interscan time, 0.5 s; and SEM factor, 10^6.

At the beginning of the desorption step the cold column warms to 220 K due to the environment. Therefore, the residuum of the matrix is desorbed in addition to very volatile trace components.

Subsequently the column is heated electrically to 670 K at 30–80 K/min. A copper–constantan thermocouple mounted at the column is used to check the temperature. Finally, the column is kept at constant temperature (670 K) for 10 min. Thus the column is activated for the next analysis.

RESULTS

Analysis of hydrogen

For the determination of trace components in hydrogen, trap temperatures between 170 and 300 K are advantageous. A 5-l volume of technical hydrogen (99%) was led through the column at room temperature. Fig. 3A shows the desorption profile of enriched fractionated trace components (total ion current and traces of ions of m/z 43, 57, 78 and 91 depending on time and scan number). MS analysis shows that most of the trace components are hydrocarbons of increasing carbon number. Fig. 3B–E shows mass spectra taken at the respective maxima of the total desorption profile indicated in Fig. 3A. The first two maxima of desorption (scans 17 and 33; Fig. 3B and C was identified to be characteristic of saturated hydrocarbons, especially propane and butane. The last desorption maximum is due to unsaturated hydrocarbons. Fig. 3D (scan 87) shows the occurrence of benzene and Fig. 3E (scan 88) toluene.

The analysis of pure hydrogen (99.999%) was carried out at a lower temperature (170 K) because the intention of this analysis was to detect more volatile trace components (*e.g.*, oxygen, nitrogen and carbon dioxide). The fractional desorption is represented in Fig. 4A. The spectra of oxygen (scan 12; Fig. 4B), nitrogen (scan 14; Fig. 4C), carbon dioxide (scan 37; Fig. 4D), benzene (scan 83, Fig. 4E) and toluene (scan 85, Fig. 4F) were recorded. A blank run without hydrogen but no calibration was carried out. Contamination originating from leaks or other sources was not observed.

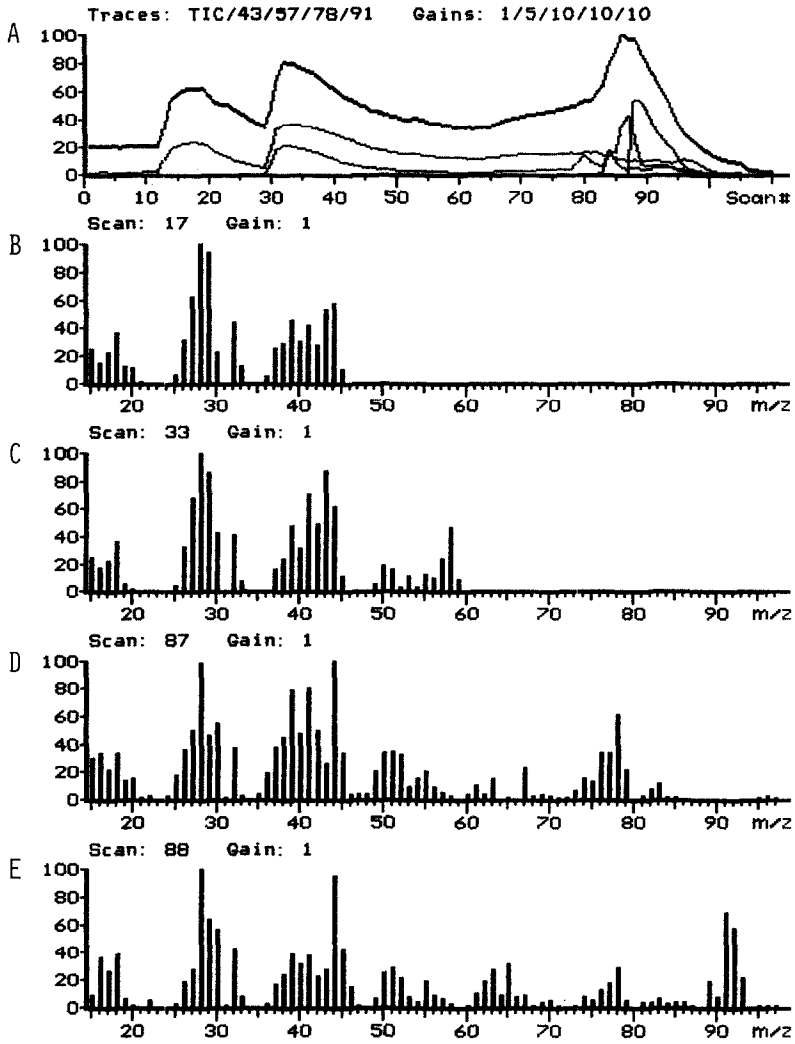

Fig. 3. (A) Desorption profile (total ion current and traces of ions depending on time and scan number) of trace components in technical hydrogen. (B) Scan 17 of the desorption profile: saturated hydrocarbons; main component, propane. (C) Scan 33 of the desorption profile: identified to be characteristic of saturated hydrocarbons; main components, butane. (D) Scan 87 of the desorption profile: identified to be characteristic of unsaturated hydrocarbons; main component, benzene. (E) Scan 88 of the desorption profile: identified to be characteristic of unsaturated hydrocarbons; main component, toluene.

Analysis of silane and phosphine

Phosphine is very toxic and silane is spontaneously flamable in air. Fortunately, our apparatus has the advantage of being a closed system. Dangerous gases may be rendered into a safe form in the waste line without problems (*cf.*, Fig. 1). The leak test and the determination of the gas flow-rate were carried out with a non-hazardous gas, *e.g.*, hydrogen or argon.

The determination of trace components in phosphine or silane is practicable at

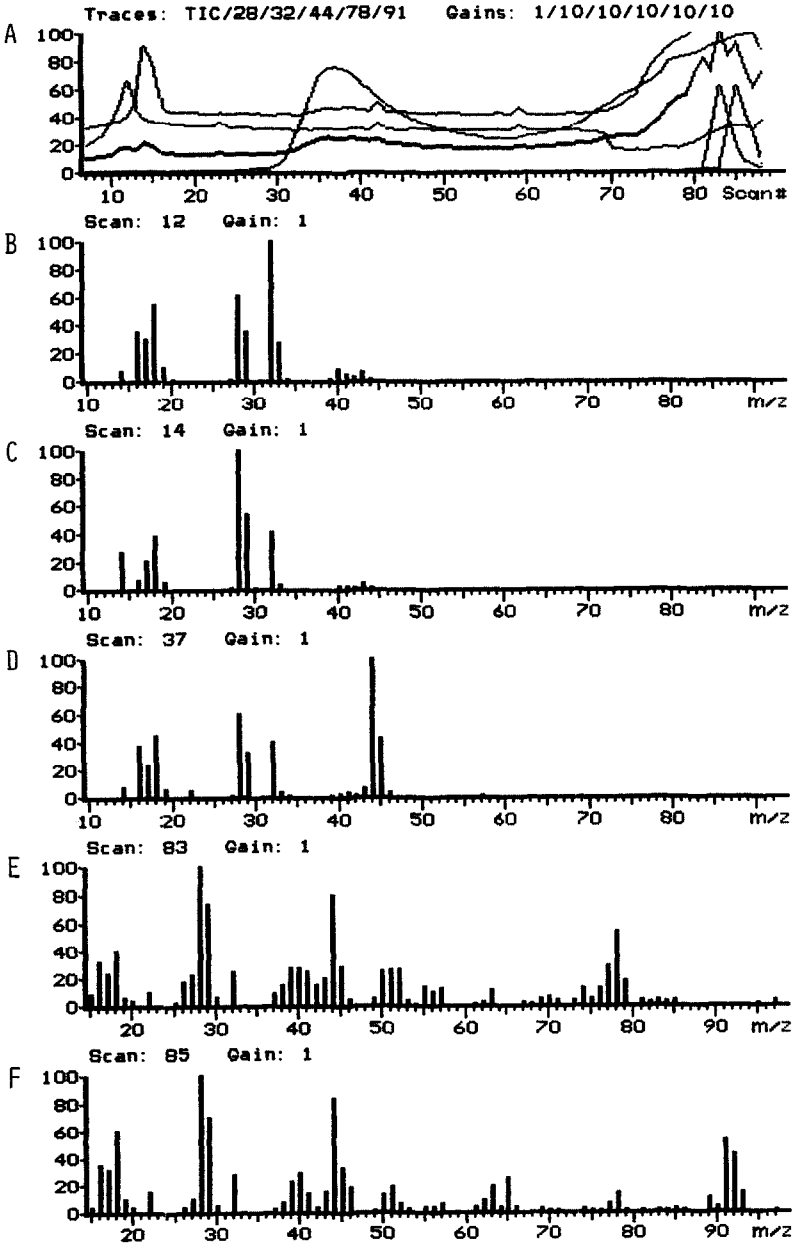

Fig. 4. (A) Desorption profile of trace components in pure hydrogen. (B) Scan 12 of the desorption profile: identified to be characteristic of oxygen. (C) Scan 14 of the desorption profile: identified to be characteristic of nitrogen. (D) Scan 37 of the desorption profile: identified to be characteristic of carbon dioxide. (E) Scan 83 of the desorption profile: identified to be characteristic of butadiene and benzene. (F) Scan 85 of the desorption profile: identified to be characteristic of toluene.

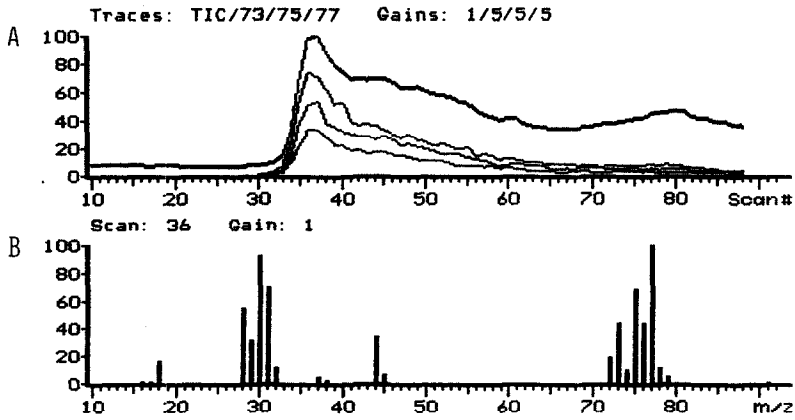

Fig. 5. (A) Desorption profile of trace components in a mixture of 10% silane in hydrogen. (B) Scan 36 of the desorption profile: identified to be characteristic of disiloxane.

room temperature, but the enrichment of, *e.g.*, oxygen or nitrogen at this temperature is not possible. In Fig. 5A the fractional desorption of enriched trace components of a mixture of 10% silane in hydrogen is shown. The maximum of desorption (scan 36) was identified to be disiloxane (Fig. 5B). A concentration of 8.7 ppm was determined without enrichment, but in analysis with enrichment the signal-to-noise ratio was 2000 times higher. In other samples of gas mixtures containing silane, disilane, chlorsilane, hexamethyldisiloxane and saturated or chlorinated hydrocarbons were found.

Mixtures of phosphine in hydrogen were analysed. Diethyl ether was identified to be an impurity (Fig. 6A). For the determination of quantitative data, a liquid mixture (5 μl) of benzene, dissolved in pentane (0.1 vol.-%), was dosed into the gas stream at the beginning of the enrichment. The mixture was exponentially diluted in this gas

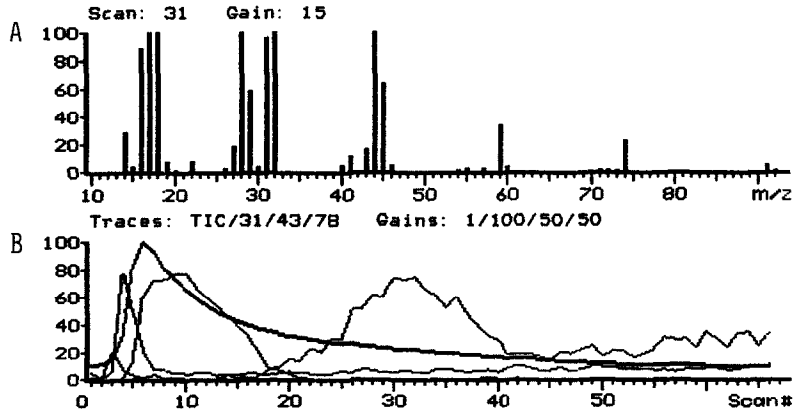

Fig. 6. (A) Determination of diethyl ether in the desorption profile of an enriched sample of 10% phosphine in hydrogen. (B) Desorption profile of enriched trace components: total ion current and traces of ions of pentane*(solvent), benzene (standard) and diethyl ether (trace) for quantitative determination; diethyl ether concentration, 5 ppm.

stream and carried into the column. Whereas pentane was not enriched effectively (maximum at scan 4 in Fig. 6B), benzene was enriched almost completely (maximum at scan 10 in Fig. 6B), allowing quantitative determination. Considering the fractionation pattern of both substances, a result of 5 ppm of diethyl ether was obtained by relating the areas of the desorption profiles of benzene and diethyl ether (*cf.*, Fig. 6A).

Other trace components occurring in phosphine–hydrogen or phosphine–argon mixtures were identified to be toluene, ethylbenzene, ethanol, tetrahydrofuran, dichloroethene or trichloroethene.

Analysis of air

Traces of dichloromethane in laboratory air, resulting from cleaning of laboratory glassware, were determined. A 150-ml volume of contaminated laboratory air was passed through the zeolite-filled column at room temperature. As a result a content of 40 ppb of dichloromethane was calculated from MS analysis (*cf.*, Fig. 7A). Remarkably, a concentration of 0.9 ppb was determined 8 h later. In the analysis of air, it is not necessary to use an external standard. The carbon dioxide in air (about 0.03%), which is enriched almost completely, may be used as an internal standard (*cf.*, Fig. 7B, scan 30, maximum of dichloromethane; scan 39, maximum of carbon dioxide). Because the intensity of the molecular peak at *m/z* 44 exceeds the dynamic range of the mass spectrometer, the isotopic peak at *m/z* 45 was used for quantification of data in the ppb range.

Optimization of parameters

Using the described apparatus for enrichment and sampling of volatile trace components in gases, various samples in our laboratory were routinely mass analysed. In normal situations unknown trace components in the ppm or ppb range should be detected. The standard addition method or external calibration should be used for accurate quantitative determination. Using microlitre sampling syringes, minimum concentrations of standards, diluted with inert solvents, were prepared and

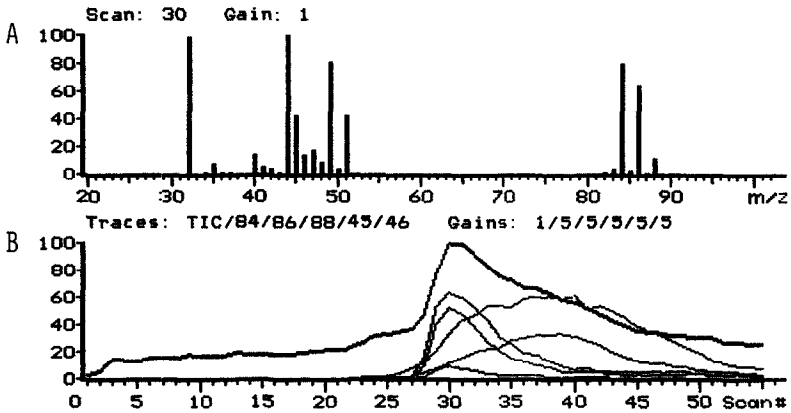

Fig. 7. (A) Determination of dichloromethane in laboratory air. (B) Desorption profile of the total ion current and traces of the ions of dichloromethane (40 ppb) and of the isotopic peaks of carbon dioxide of *m/z* 45 as standard.

dosed for quantitative analysis. The following parameters were varied to achieve an optimum enrichment: the adsorbent, the sample flow-rate, the maximum sample volume and the geometry of the packed column.

Molecular sieves (3A, 4A and 13X) and microporous carbon black were used as adsorbents. Optimum enrichment and fractionation by desorption were achieved using zeolite 4A. Owing to its polarity, hydrocarbons containing heteroatoms, *e.g.*, chlorinated hydrocarbons, alcohols or ethers, are effectively enriched.

The shape of the desorption profile of various substances is determined by diffusion processes in the pore system. Impurities with a larger effective molecular diameter than that of pores of the molecular sieve (*e.g.*, aromatic hydrocarbons) were enriched in its secondary pore structure. Their desorption is faster and their desorption profile is smaller.

For enrichment of non-polar trace components, a non-polar adsorbent should be used. Microporous carbon black was tested for the determination of trace components in hydrogen. Detection limits below 1 ppm cannot be achieved, because high blank values of hydrocarbons falsify the analysis.

The sample flow-rate by frontal analysis determines the formation of impurity adsorption zones in the packed column. The adsorption of trace components is incomplete at very high flow-rates while the diffusion in the column disturbs the sharp adsorption zones at very low flow-rate. Small adsorption zones allow small desorption profiles during fractional desorption with high signal-to-noise ratios. In our experiments sample flow-rates between 10 and 100 ml/min were used.

The maximum sample volume that can be used for an analysis depends on the kind of matrix and adsorbent, the amounts of adsorbent and trace components and the temperature at which the enrichment procedure was carried out. The typical sample volume is between 50 and 1000 ml and is limited by the adsorptive capacity of the column.

Packed columns of various length and diameter were tested. To guarantee a desorption peak of an intensity that does not exceed the dynamic range of the mass spectrometer, the amount of adsorbent must be minimized. Columns packed with 0.05 0.8 g of zeolite were used. A compromise between the length and the diameter of the columns used on the one hand and the optimum sample flow-rate during enrichment on the other must be found. Columns of diameter 0.7–2.0 mm and of length 40–200 mm were tested.

Analysis was carried out recording repeatedly single mass spectra during the desorption. Blank runs without the sample or runs with comparable samples are ususally carried out before and after the analysis to monitor contamination effects. The detection limit of the method was determined using dynamically mixed test gases composed of cryogenically cleaned pure hydrogen and benzene. To dose the minimum amount of benzene it was strongly diluted in pentane. A detection limit of 0.5 ppb of benzene in hydrogen was attained.

CONCLUSIONS

A packed chromatographic column was directly coupled to a mass spectrometer and was used for the adsorptive enrichment of trace components in gases and for fractional desorption of the enriched trace components. Cryopumping was used for

splitless adjustment of the partial pressure of the trace components between enrichment and analysis. This method, based on thermal desorption under high vacuum, is more sensitive than conventional purging methods. Detection limits in the lower ppb range were achieved. Sample handling operations are simpler than in coupling of adsorptive enrichment with GC–MS.

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