

THERMAL DESORPTION OF ATMOSPHERIC ORGANIC POLLUTANTS ENRICHED ON CHARCOAL

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ARBEITSHYGIENEINSPEKTION DES RATES DER STADT GERA, HUMBOLDSTRASSE 11, 6500 – GERA, G.D.R.

* ARBEITSHYGIENEINSPEKTION DES RATES DES BEZIRKES GERA, CLARA-ZETKIN-STRASSE 19, 6500 – GERA, GDR.

A technique of thermal vacuum desorption of charcoal, used in passive dosimeters to enrich organic pollutants of toxicological importance, is described. It combines the advantages of the classic procedure of using highly active charcoal followed by solvent desorption and the environmental one-step procedure of analyzing the whole thermally desorbed sample. For pollutants such as trichloroethylene, tetrachloroethylene, ether, benzene and ethanol, the recovery and reproducibility are satisfactory. The unexpected decomposition of halothane and ethylacetate at higher temperatures is caused by the catalytic activity of the charcoal, but this can be tolerated under constant operating conditions.

Passive and diffusion-controlled sampling methods with charcoal as adsorbent are increasingly used to solve different problems relating to industrial atmospheres [1]. Due to the high adsorption activity of charcoal, a complete recovery of the substances can be achieved only by solvent desorption [2].

The advantages of this method are repeatability, high separation efficiency, recovery of heavy compounds and fast analysis, but the solvent toxicity, the broad solvent peak in the gas chromatogram and the low recovery of polar compounds impede its exclusive application. If an adsorbent with a moderate activity, e.g. Tenax–GC or Chromosorb, is used to enrich the pollutants, nearly complete desorption is possible at a high temperature, the above disadvantages thereby being overcome. To ensure the high sensitivity necessary for environmental analysis, usually the whole sample is purged into the gas chromatograph [3].

Because of the higher pollutant concentrations in industrial atmospheres, and the necessity to be able to repeat an analysis, a thermal vacuum desorption method has been developed which combines the application of charcoal and storage of the desorbed substances in an appropriate vessel for numerous gas chromatographic analyses.

Experimental

Passive dosimeters of the DOL-S type [4] contain 150 mg charcoal (Aktivkohle AS, VEB Kunstfaserwerk "Friedrich Engels", Premnitz, GDR) with a grain size of 0.4–1.0 mm. After opening of the dosimeter, the adsorbent is applied as a homogeneous layer onto the desorption tube frit. This tube (volume about 25 cm³) is then closed with silicone rubber containing a silicone-stoppered capillary and connected via a stopcock to an evacuated gas sampling tube (volume about 500 cm³). The desorption tube prepared in this way is introduced into the heating cylinder so that the charcoal is in the zone of constant temperature. After 1.5 min of heating, the stopcock between the sampling and desorption tubes is opened (the pressure in the system is about 15 Pa), followed by removal of the stopper from the capillary. The inflowing air or nitrogen purges the desorbed pollutants into the sampling tube. After 40 s of pressure equilibration, the sample is ready for GC-analysis. Further details of the device are given elsewhere [5].

The calibration was performed by injection of defined amounts of the substances (pure, diluted or in a mixture) into a well-stoppered small glass bottle containing 150 mg charcoal. After about 15 h of equilibration, the sample is ready for further manipulation. The following substances or mixtures were investigated:

- Trichloroethylene – tetrachloroethylene;
- diethyl ether – ethanol – 1-propanol – halothane (2-bromo-2-chloro-1,1,1-trifluoroethane);
- n-heptane – benzene – toluene – ethyl acetate;
- dichloromethane.

Results and discussion

Table 1 gives the desorption temperatures, the ranges of calibration and the corresponding recoveries of industrial pollutants which are relevant due to their toxicity. The system trichloroethylene – tetrachloroethylene was thoroughly investigated because of its widespread application as a degreaser and textile cleanser. In the routine technique, a desorption temperature of 340° was applied. At a lower temperature, the recoveries of both compounds are far from 100%. They can be improved by increasing the temperature, but at about 340° trichloroethylene starts to decompose. Due to the satisfactory combination of recovery and reproducibility, this temperature was selected. For

Table 1 Desorption temperatures (Θ , °C), ranges of calibration (V , μl) and recoveries (R , %) of some air pollutants

Compound	Θ , °C	V , μl	R , %
trichloroethylene	340	0.15– 1.50	90 \pm 3
tetrachloroethylene	340	0.15– 1.50	84 \pm 4
diethylether	240	0.05– 0.25	90 \pm 4
halothane	240	0.05– 0.25	50 \pm 4
ethanol	240	0.05– 0.25	95 \pm 2
1-propanol	240	0.35– 1.75	85 \pm 4
dichloromethane	265	0.50– 2.50	85 \pm 4
benzene	340	0.03– 0.17	92 \pm 3
n-heptane	340	0.20–10.00	90 \pm 3
toluene	340	0.20– 1.00	80 \pm 4
ethylacetate	340	0.50– 2.50	73 \pm 5

these two compounds, as well as for the others listed in Table 1, an average calibration line was calculated, using all the data of repeated calibration experiments. In all cases the correlation coefficient of the resulting line was better than 0.94, and in the middle of the range of calibration there is a confidence band of about 10%. This system is discussed in detail in [5]. The system diethyl ether – halothane – ethanol – 1-propanol is a relevant one in operating theatres. The simultaneous quantification was more difficult because of the thermal instability of halothane. Even at the relatively low temperature of about 200°, a decomposition product, obviously a less polar halogenated hydrocarbon, became visible as a preceding peak in the chromatogram. On the other hand, a high temperature was necessary to desorb a sufficient amount of the alcohols. Desorption at 240° was found to represent the optimum. Of course, the decomposition is a more serious problem at lower concentrations, which is why the calibration curve is not linear over the full range. The main reason for the decomposition of halothane is not the temperature, but the catalytic activity of the charcoal. This was proved by the dosage of halothane onto glass-wool in the absence of charcoal. In this case fission products could not be observed, the recovery was about 94% and a linear calibration curve resulted. Extended measurements in operating theatres showed a good agreement between passive sampling with DOL-S dosimeters and subsequent thermal desorption and active sampling with gas tubes [6]. The more polar the pollutant, the more difficult is the desorption by an eluent, and consequently insufficiently

low recoveries were reported [1, 7]. In comparison, the thermal desorption described here is a tailor-made technique to quantify such substances, as illustrated by the high recoveries in Table 1. The alcohols were stable up to high temperatures and a linear calibration curve resulted over the full range.

In the system n-heptane – benzene – toluene – ethyl acetate, a temperature of 340° was found to ensure a high recovery for both benzene and n-heptane and a satisfactory recovery for toluene. At this temperature, ethyl acetate decomposes slightly to form ethanol. This circumstance somewhat restricts the application of the method if ethyl acetate and ethanol occur simultaneously in the air of a working room. To obtain genuine results, a lower desorption temperature has to be selected to guarantee that no decomposition product of ethyl acetate falsifies the findings for ethanol.

It is obvious that the optimum desorption temperature is a compromise between sometimes contrary effects such as desorption and decomposition. The final decision depends on the actual constituents of the sample.

References

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Zusammenfassung – Eine Methode zum Anreichern toxikologisch bedeutender organischer Luftverunreinigungen durch thermische Vakuumdesorption von Aktivkohle nach dem Einsatz in passiven Dosimetern wird beschrieben. Die Methode kombiniert die Vorteile der klassischen Prozedur unter Verwendung hochaktiver Kohle mit nachfolgender Desorption durch Lösungsmittel einerseits mit denen der "Umwelt-Analyse" der gesamten desorbierten Probe in einem Schritt andererseits.

Für Luftverunreinigungen wie Trichlorethylen, Tetrachlorethylen, Ether, Benzen und Ethanol werden ausreichende Wiedergewinnung und Reproduzierbarkeit ermittelt. Die unerwartete Zersetzung von Haloathan und Ethylacetat bei höheren Temperaturen wird auf die katalytische Wirkung der Aktivkohle zurückgeführt. Sie kann unter konstanten Versuchsbedingungen jedoch toleriert werden.

РЕЗЮМЕ — Описан метод вакуумной термической десорбции активированного угля, используемого в пассивных дозиметрах для улавливания токсических органических веществ. Метод включает преимущество классического метода с использованием высокоактивированного угля с последующей десорбцией растворителем и охватывает одностадийный метод анализа всего термически десорбированного образца. Воспроизводимость и предел обнаружения являются приемлемыми для таких органических веществ, как три- и тетрахлорэтилен, эфир, бензол и этанол. Наблюдаемое разложение галоэтана и этилацетата при более высоких температурах обусловлено каталитическим действием угля.