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INVESTIGATION OF THE POSSIBLE OXIDATION BY OZONE OF ORGANIC SUBSTRATES ADSORBED ON TENAX

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SUMMARY

An investigation has been performed into the occurrence of oxidation by ozone of organic compounds adsorbed on Tenax. No oxidation has been observed for ethylbenzene, 1-hydroxyethylbenzene, acetophenone, *n*-octanol and *n*-octanal at room temperature (sampling conditions), nor at elevated temperatures (heat-desorption conditions).

INTRODUCTION

Over the past few years Tenax GC[®], a porous polymer originally developed as packing material for gas chromatography (GC), has widely been applied as an adsorbent in environmental analyses. Due to its unique properties such as stability up to 375°C and very low water retention, Tenax is very suitable for thermal desorption analyses.

By combining thermal desorption with capillary GC an analytical system is obtained which is capable of detecting very small amounts of pollutants (*ca.* 10⁻⁹ g) with a reasonable selectivity. The low concentration of the substances to be determined makes high demands on the purity of the sampling material. Moreover, strict precautions during handling, conditioning and storage are necessary to obtain good blank chromatograms of an adsorption tube^{1,2}.

Besides the problem of obtaining a good blank, the problem of reactions of the trapped material in the adsorbed state has been raised^{3,4}. It is obvious that organic species trapped on an adsorbent are particularly sensitive to reagents with which they react in the gas or liquid phase, although the reaction velocity or reaction pathway may be altered. For instance, hydrolysis³, halogenation or oxidation has been reported⁴. Although these reactions cannot be prevented, appropriate choice of the adsorbent may decrease their occurrence. In the case of hydrolysis, for instance, it has been shown that the choice of Tenax as adsorbent allows the analysis of the hydrolytically very unstable bis(chloromethyl) ether even in air at a very high humidity. Due to the low affinity of Tenax for water, the apparent hydrolysis velocity is slow enough to allow an analysis in the ppb range with satisfactory precision^{2,3}.

In general, however, one should be aware that adsorbed species can react with

each other, or with compounds that are present in the air and sucked through the tube without being adsorbed, thus giving analytical data which are not representative of the original sample. These reactions may take place either at room temperature during sampling, storage before analysis or during the thermal desorption step.

The omnipresence of ozone raises the question of the importance of the oxidation of organic species during sampling or subsequent analysis. Since experimental work in our laboratory showed that ozone is trapped on Tenax, an investigation has begun into the possible danger of ozone oxidation of organics adsorbed on Tenax.

EXPERIMENTAL

Glass adsorption tubes (4.8 mm I.D.) containing 250–350 mg Tenax (60–80 mesh) were employed. Conditioning of the traps was performed by washing with 5 ml *n*-hexane, the solvent used for elution, followed by heating at 270°C for 15 h under a flow of purified N₂, 6 ml/min. The tubes were cooled without disconnecting them from the nitrogen supply.

The conditioned tubes were spiked with *n*-hexane solutions of ethylbenzene, acetophenone, 1-hydroxyethylbenzene, *n*-octanol and *n*-octanal. The solvent was removed by a purge with about 2 l of nitrogen. Solvent elution of the traps was performed with about 4 ml of *n*-hexane, after which the volume of the eluent was made up to 5 ml.

Heat desorption was carried out with a tandem tube obtained by combining two adsorption tubes having ground joints. Each spiked tube was heat-desorbed at 250°C for 15 min under a flow of nitrogen (20 ml/min), after which the released volatiles were trapped on a second adsorption tube, kept at room temperature. The second tube was analysed by solvent elution.

The ozone oxidation experiments were performed by sucking 6–9 l air containing 1.0–1.3 mg of ozone per m³ through the tubes. The ozone concentration of the air was determined by iodometric titrations and/or Dräger indicator tubes. The ozone was prepared with a Fischer ozone generator Type 501; the final concentration was obtained with a gas mixing system from Wösthoff (Bochum, F.R.G.).

The eluents of the adsorption tubes were analysed by GC, using a capillary column (20 m × 0.28 mm I.D. SE-30, film thickness $d_f = 0.2 \mu\text{m}$), mounted in a Carlo Erba Fractovap 4160 provided with a cold on-column injector.

RESULTS AND DISCUSSION

In Table I the recoveries of several compounds from both solvent elutions and the combined thermal desorption–solvent elution are given. The recoveries are very satisfactory in the concentration range studied.

By placing a Dräger ozone indicator tube in series with a Tenax trap it has been demonstrated that ozone is efficiently trapped on Tenax.

When an ozone concentration of 13 mg/l was applied, after a few minutes a spontaneous ignition of the polymer was observed. In the volatiles formed during this violent oxidation reaction no significant amounts of acetophenone were detected. This invalidates the rather widespread opinion that the acetophenone often observed in environmental samples originates from oxidized Tenax.

TABLE I
PERCENTAGE RECOVERIES OF SEVERAL SUBSTRATES

Analytical procedure	Compound	Amount (μg)		Recovery (%)
		Spiked	Found	
Solvent elution*	Ethylbenzene	945	911	97
	Acetophenone	947	948	101
	1-Hydroxyethylbenzene	1145	1145	100
	<i>n</i> -Octanol	983	962	98
	<i>n</i> -Octanal	986	1003	102
Thermal desorption-solvent elution**	Ethylbenzene	1122	1111	99
	Acetophenone	11.64	12.45	107

* Adsorption tube contained 350 mg Tenax.

** Adsorption tube contained 250 mg Tenax.

To investigate the possibility of oxidation by ozone of organic substrates adsorbed on Tenax during sampling, experiments have been performed in which the spiked tubes were analysed by solvent elutions after treatment with ozone. The results are given in Table II. In these experiments an ozone concentration of 1 mg/cm^3 was used, which is fifteen times higher than reported for the most strongly polluted industrial area in The Netherlands. As shown in Table II, no oxidation products could be detected. Using a detection limit of $2 \mu\text{g}$ and a substrate/ozone molar ratio of 50:1, this means that if any oxidation had taken place less than 10% of the ozone had reacted. Moreover, the recoveries observed for the spiked substrates do not deviate from those obtained without ozone treatment. So, the results demonstrate that a number of organic compounds with different reactivities towards oxidation, in a concentration corresponding to about 100 ppm in air, are oxidized by ozone to

TABLE II
RECOVERIES OF SEVERAL ORGANIC SUBSTRATES SPIKED ON TENAX AND THE AMOUNTS OF THEIR OXIDATION PRODUCTS AFTER OZONE TREATMENT AND SUBSEQUENT SOLVENT ELUTION

Compound	Amount (μg)		Recovery (%)	Possible oxidation product**	Amount of ozonized air (1)***
	Spiked*	Found			
Ethylbenzene	945	949	100	1-Hydroxyethylbenzene Acetophenone	8.5
Acetophenone	947	975	103		8.7
1-Hydroxyethylbenzene	1145	1113	97	Acetophenone	9.0
<i>n</i> -Octanol	983	1007	103	<i>n</i> -Octanal, octanoic acid	7.5
<i>n</i> -Octanal	986	918	93	Octanoic acid	8.0

* Adsorption tube contained 350 mg Tenax.

** Lower limit of detection about $2 \mu\text{g}$, except for octanoic acid which was detected at a level of 20 μg .

*** Flow through the sampling tube, ca. 300 ml/min; ozone concentration, 1 mg/m^3 .

TABLE III

RECOVERY OF SOME ORGANIC COMPOUNDS SPIKED ON TENAX AFTER OZONE TREATMENT AND SUBSEQUENT HEAT TREATMENT

Compound	Amount (μg)		Recovery (%)	Amount of ozonized air (l) ^{***}
	Spiked [*]	Found ^{**}		
Ethylbenzene	1122	1156	103	6.1 [§]
	1122	1112	99	6.0 [§]
	1122	1073	96	6.4
	11.64	10.10	87	6.0
	11.64	10.69	92	6.0
<i>n</i> -Octanol	983	913	93	5.7
	9.56	9.56	100	6.2

* Adsorption tube contained 250 mg Tenax.

** No oxidation products of the spiked compounds could be detected.

*** Flow through the sampling tube, ca. 300 ml/min.

§ Ozone concentration 1.3 mg/m³ except where stated. Ozone concentration 1 mg/m³.

an extent of $\leq 0.2\%$ during sampling, even when the ozone concentration is much higher than under practical conditions.

To investigate whether oxidation by ozone takes place at high temperatures, traps loaded with organic substrates and ozone have been heat-desorbed. In a number of these experiments the substrate/ozone molar ratio was changed from 50:1 to about 1:2. The results obtained are given in Table III. Just as in the case of the room temperature experiments, no oxidation products could be detected after heat treatment of adsorption tubes loaded with ozone and ethyl benzene or *n*-octanol, even at substrate concentrations corresponding to about 1 ppm in air and a substrate/ozone molar ratio of about 1:2.

So, no evidence could be obtained for the oxidation by ozone of organic substrates adsorbed on Tenax during sampling or during thermal desorption. Even rather sensitive compounds such as *n*-alcohols or aldehydes were not affected under the applied oxidation conditions.

A possible explanation for the presence of high levels of oxygenated compounds in environmental samples which are sometimes accompanied by high ozone levels might be a photochemical oxidation by ozone in the gas phase.

Although this work has provided evidence that oxidation of adsorbed organic substrates by ozone does not seem to play an important rôle on the adsorbent Tenax, problems may occur when several reactive species are trapped together on an adsorption tube. The occurrence of all kinds of reaction, not only oxidation or ozonolysis, between trapped species and/or reactants present in air which are not trapped can seriously affect the representativeness of the air sample.

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