



Project Summary

Optimization of GC/MS Based Tenax Collection Method for Toxic Organics

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The sampling of vapor-phase organics in the presence of reactive inorganics using the Tenax GC sampling cartridge was investigated. To differentiate between pollutants in air and those formed from *in situ* artifact reactions, deuterated organics were employed in both laboratory and field experiments, and any subsequent artifact products were detected by capillary gas chromatography/mass spectrometry/computer [(GC)²/MS/COMP] techniques. Artifacts produced by Tenax GC itself and by reactions between adsorbed species were investigated using statistical methods.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The characterization and measurement of minute amounts of hazardous compounds in ambient air has, for many years, been seriously hampered by the lack of reliable sampling systems. Techniques have been developed to concentrate organic vapors from large volumes of atmosphere and to transfer the collected vapors to an analytical system.

There is, however, a paucity of experimental data concerning artifact studies on collection devices for vapor-phase organics. Investigators have had a propensity for accepting the viability of the collection step prematurely while emphasizing development of other steps in analytical

procedures. In fact, the literature is replete with analytical methods for analysis of a few vapor-phase components in complex mixtures using various instrumental methods. Nonetheless, it should be noted that none of these procedures can be considered superior since the collection method is a common denominator among all the analytical methods, and appears to be the weak link.

With the elucidation of nitrosamine presence in ambient air, serious consideration was given to potential artifact formation during collection. In fact, a plethora of collection methods for nitrosamines occurred. Artifacts associated with cryogenic traps were readily apparent, and modifications ensued which eventually lead to using a sorbent cartridge impregnated with sulfamic acid to inhibit the *in situ* nitrosation of secondary amines.

An approach to detecting, identifying, and quantifying halogenated hydrocarbons in ambient air has involved using a Tenax GC cartridge combined with high resolution gas chromatography/mass spectrometry/computer [(GC)²/MS/COMP] analysis. The primary concern was to use a Tenax GC sorbent that has been previously employed for collecting vapor-phase organics in ambient air. Since the Tenax GC cartridge may concentrate reactive compounds from an atmosphere containing, for example, ozone (O₃), nitrogen oxides (NO_x), molecular halogen such as chlorine (Cl₂) and bromine (Br₂), *in situ* formation of artifact products may occur, even though inorganic gases do not appreciably accumulate on the sorbent. Preliminary studies indicated that a more in-depth study was needed.

The objectives of this research program were: (a) to examine the potentially trouble-



some chemical group types that exhibit reactivity with the commonly occurring inorganic gases in ambient air; (b) to conduct a series of controlled laboratory experiments to determine the extent, if any, of artifact problems associated with the direct interaction of these inorganic gases with Tenax GC itself; (c) to evaluate the artifact problems, if any, associated with organics on Tenax GC in the presence of atmospheric concentrations of inorganic gases; (d) to develop a way to minimize potential artifacts if they exist; and (e) to evaluate and apply potential corrective measures that minimize artifact production under field sampling conditions.

Effects of Ozone and Nitrogen Oxides

A 2³ factorial experiment was planned to assess the ozone/nitric oxides/humidified air (O₃/NO_x/H₂O) combination effect on Tenax. For quantitative analysis, the gas chromatographic system was calibrated with external standards. The identity of the major Tenax GC decomposition products was established by GC/MS methods.

Clean, "virgin" Tenax GC cartridges were exposed to air containing O₃/NO_x/H₂O, and pertinent information regarding Tenax GC cartridge exposure was obtained.

The most important Tenax GC decomposition products were benzaldehyde, acetophenone, and phenol, indicating ozonolysis to be the polymer's major chemical reaction. After breakdown of the polymer backbone, further reactions of the primary degradation products lead to the relatively stable compounds actually detected. This result corroborates the many reports citing that interaction with atmospheric O₃ is the main degradative mechanism of polymeric materials.

Humidity had a strong effect. This is important since more attention should be given to artifact formation from Tenax GC when sampling air with a high relative humidity.

The ozone concentration and NO₂ concentration behaved additively. The three major decomposition products were found in easily detectable and dosable quantities, even in "clean" cartridges. It appears, however, that analysis for any of the three major decomposition products at levels below 100 ng/L with Tenax GC sampling is not possible without taking special precautions.

Effects of Sulfur Oxides

Tenax GC cartridges were exposed to 30 L of air containing O₃, sulfur oxides (SO_x), and NO_x at different humidity levels.

The major Tenax GC decomposition products were confirmed but no compounds that could identify the presence of SO_x could be detected.

Effects of Chlorine

Tenax GC cartridges were exposed to O₃, Cl₂, and humidified air. The same major decomposition products were observed.

Effects of Tenax GC Aging

Substantially lower levels of decomposition products were found in sampled air containing SO_x and Cl₂. This effect was not related to the nature of the reactive inorganic gas (in all experiments O₃ was present, the main factor in polymer degradation), but to the history of the Tenax GC cartridge.

Recycled Tenax GC cartridges were used in the SO_x and Cl₂ series. The hypothesis that cartridge history was the main factor in the total quantity of degradation products was tested using the same cartridge exposed to 30 L of air in 30 min, with 100 ppb O₃, 150 ppb NO_x, and 60% humidified air. The quantities of degradation products decreased by an order of magnitude after five analysis cycles.

Artifact Products from Adsorbed Compound Reactions

Tenax GC cartridges (sorbent bed dimensions, 60 mm length x 13 diameter) were loaded with d₁₀-cyclohexene or d₅-ethanol. For quantitation, 2-fluorobiphenyl was used as an internal standard. Standard solutions of d₁₀-cyclohexene and 2-fluorobiphenyl were prepared by weighing and dissolving in pure methanol.

The loaded cartridges were exposed to an air flow containing inorganic gases in the concentrations listed below (inorganic gases are potential generators of artifacts by reaction with the adsorbed d₁₀-cyclohexene:

| | |
|----------------------------------|-------------------------------------|
| Cl ₂ | maximum concentration, 564 ppb |
| O ₃ | maximum concentration, 1,000 ppb |
| NO/NO ₂ | maximum concentration, 500 ppb |
| SO ₂ /SO ₃ | maximum concentration, 400 ppb |
| humidified air | 50% at 25°C |

For the low concentration range of reactive inorganic components in the sampled air, no deuterated cyclohexene product was detected. At higher chlorine concentrations, d₁₀-dichlorocyclohexane was

found. A nondeuterated dichlorocyclohexane was also identified in the same samples, probably from Cl₂ reacting with cyclohexene (a contaminant). Deuterated compounds derived from d₅-ethanol and contaminants typical for Tenax GC were identified as early eluting compounds (i.e., contaminants). The potential oxidation products - acetaldehyde and acetic acid - were not detected during GC/MS analysis.

Artifact Inhibition with Impregnated Filters

A series of filters was impregnated with various reducing agents for O₃. The sodium thiosulfate impregnated glass fiber filters appear to be the best in quenching ozone. Relatively good - but less spectacular - results were obtained for NO₂ quenching.

The inclusion of sodium lauryl sulfate in the impregnating solution was proposed with the view that a surfactant would lower the solution's surface tension and allow a better wetting of the filter, thus improving overall performance. This behavior was observed for the hydrophobic Teflon filters, which cannot be impregnated uniformly with reducing agents in the absence of surfactants.

Studies on Artifact Problems Under Field Sampling Conditions

The results from laboratory experiments suggested two types of filters for best overall performance: glass fiber filters impregnated with sodium thiosulfate and Teflon filters impregnated with sodium thiosulfate/sodium lauryl sulfate. The major objective in designing the field experiments was to test these two types of filters for inhibition of Tenax GC decomposition and for reduction of *in situ* reactions of adsorbed compounds.

The deuterated compounds selected and the possible artifactual reactions were as follows:

- (1) d₁₀-cyclohexene: chlorination and oxidation;
- (2) d₆-benzene: aromatic substitution and oxidation; and
- (3) d₈-dioxane: oxidation (peroxide formation).

In conducting field experiments, two sorbent cartridges were run parallel. One cartridge was protected by an impregnated filter and the other cartridge by an unimpregnated filter.

The objectives using (GC)²/MS/COMP analysis were as follows:

- (1) assess the recovery of deuterated compounds from exposed cartridges;

- (2) identify reaction products of deuterated compounds; and
- (3) quantify adsorbed volatile organic compounds, i.e., determine the trends in the quantities found, relative to using impregnated filters.

The statistical analysis of aromatic compound data was restricted to the higher concentration range, i.e., more than 300 ng benzene/cartridge, in order to avoid unaccountable contamination effects. Only for toluene was a positive difference statistically significant. The loss of the aromatic compounds by further reaction of adsorbed species was, therefore, negligible at the level of sensitivity of the analytical method.

The following were excluded from the statistical analysis of the halogenated compound data:

- (1) 1,2-dichloroethane, due to the high concentration level in air;
- (2) 1,2-dibromoethane, since it is practically absent; and
- (3) carbon tetrachloride and dichlorobenzene, which are present at very low concentrations.

The statistical analysis was restricted to the higher concentration range for the halogenated compounds as well (same Tenax cartridge as for aromatics).

The collection of chloroform and trichloroethane data was erratic and, therefore, useless in these experiments. For trichloroethylene, a positive difference was statistically significant four times, and for tetrachloroethylene, only once. Again, there was some evidence that the impregnated filter was preventing sample loss by further reaction of the adsorbed compound if it was relatively reactive.

It was highly significant that the evidence for sample loss by artifact reaction was positive only for unsaturated compounds (cyclohexene, trichloroethylene, tetrachloroethylene), which were more reactive toward O₃.

The phenol data were also unreliable. Due to their strong acidic nature, phenol and acetic acid are subject to serious limitations in trace analysis by chromatographic methods, the best deactivated capillaries bind significant quantities irreversibly.

Conclusions and Recommendations

- (1) The main artifacts produced from Tenax GC were benzaldehyde, acetophenone, phenol, *α*-hydroxyacetophenone, acetic acid, and ethylene oxide.

- (2) The main factors determining the quantities of artifacts generated were, in order of decreasing importance, as follows:

- (a) O₃ concentration of sampled air;
- (b) Tenax cartridge age;
- (c) humidity of sampled air;
- (d) concentration of NO_x; and
- (e) concentrations of other reactive compounds (SO_x, Cl₂).

- (3) Artifact reactions of adsorbed species were found to be:

- (a) relatively unimportant for aromatics and saturated halogenated compounds; and
- (b) significant for more reactive compounds, e.g., unsaturated compounds such as trichloroethylene and tetrachloroethylene.

- (4) Sodium thiosulfate impregnated filters were found to be:

- (a) effective in artifacts generated by Tenax GC itself; and
- (b) effective in reducing artifact reactions of reactive adsorbed species.

Use of sodium thiosulfate impregnated glass fiber filters for sampling with Tenax

GC cartridges is strongly recommended.

Based on the results of laboratory and field experiments on artifact formation, three important recommendations are made:

- (1) Sodium thiosulfate impregnated glass fiber filters should be used, with an expected improvement in these characteristics:

- (a) collection efficiency of compounds reactive to O₃ (e.g., unsaturated compounds); and
- (b) Tenax GC sorbent stability, which will result in fewer artifact products.

- (2) Selection of the sampling volume must consider the air's humidity (80 to 100% relative humidity), thereby avoiding excessive artifact formation, and, at the same time, early breakthrough for the more volatile components sampled.

- (3) If the quantities found for benzaldehyde, acetophenone, and phenol are more than 1,000 ng/cartridge, quantitation for these compounds can be conducted.

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Kenneth Krost is the EPA Project Officer (see below).

The complete report, entitled "Optimization of GC/MS Based Tenax Collection Method for Toxic Organics," (Order No. PB 83-229 476; Cost: \$13.00, subject to change) will be available only from:

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