

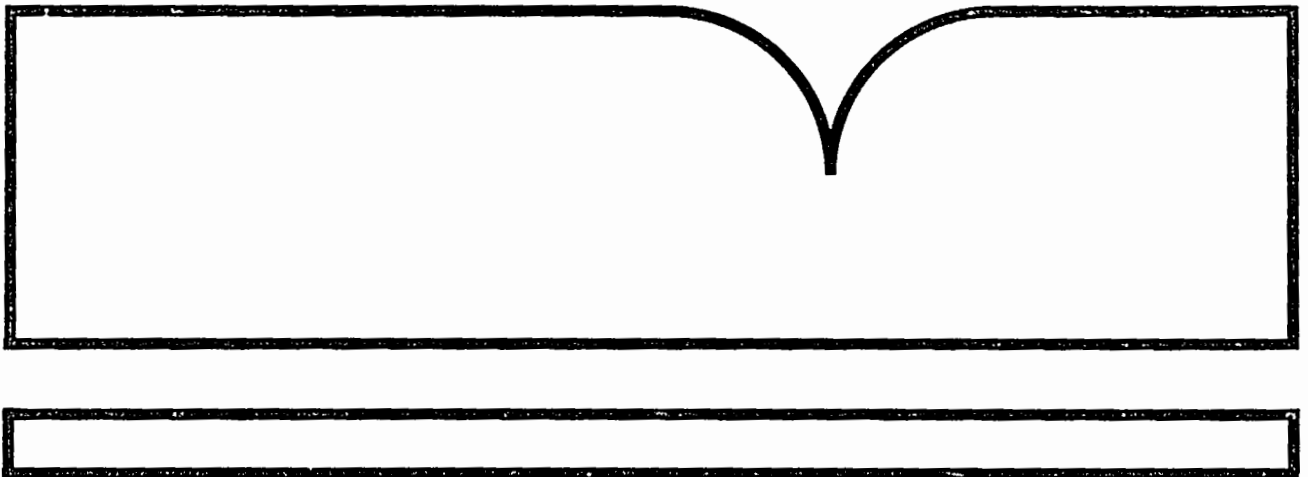
Cleanliness of Common Air Sampling Sorbents for
Application to Phenolic Compounds Measurement Using
Supercritical Fluid Extraction

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**CLEANLINESS OF COMMON AIR SAMPLING SORBENTS
FOR APPLICATION TO PHENOLIC COMPOUNDS MEASUREMENT
USING SUPERCRITICAL FLUID EXTRACTION**

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ABSTRACT

The trace-level measurement of phenolic compounds in the ambient air is complicated by the acidic and polar nature of the compounds especially during recovery from the sampling medium. Recently, supercritical fluid extraction (SFE) has been proposed as an alternative extraction method to Soxhlet extraction or thermal desorption to achieve more efficient recoveries. For such methodology to become practical, the candidate sorbents must first be tested for stability and cleanliness under SFE conditions. This paper describes exploratory research results of background contamination tests and cleanup properties of some common air sampling sorbent media with respect to future application to phenolic compounds monitoring.

INTRODUCTION

SFE offers the following advantages over more traditional extraction methods such as Soxhlet: 1) less expensive in terms of solvent purchase and disposal, 2) less harmful to the environment, 3) less time consuming in sample preparation, and 4) equivalent or better recoveries to traditional methods. It is for these and other desirable characteristics that SFE has become an increasingly popular alternative to other extraction techniques.¹⁻⁵ It also makes an attractive alternative means of cleaning and extracting sorbents used in air monitoring.

This work describes preliminary results of clean up properties and contaminants in these sorbents. Also investigated were the effects of storage and exposure to ozone^{6,7}.

EXPERIMENTAL PROCEDURE

Sorbents

The sorbents used in this work were Tenax-GC, Tenax-GR (Alltech Assoc., Inc., Deerfield, IL), XAD-2, and Carboxen 563 (Supelco, Bellefonte, PA). For SFE extractions the following amounts of each sorbent were used: Tenax-GC, 0.2g; Tenax-GR, 0.4g; XAD-2, 0.4g; Carboxen 563, 0.6g. For Soxhlet extractions the following amounts of sorbent were used: Tenax-GC, 0.6g; Tenax-GR, 1.0g; XAD-2, 2.0g; Carboxen 563, 1.0g.

SFE conditions

Extractions were performed using a system that included two Isco pumps (models 260D and 100D), a Lee Scientific oven (model 501), stainless steel tubing, and deactivated fused silica restrictors (Polymicro Technologies, Phoenix, AZ). A sample of each sorbent was placed in a

clean 1 mL stainless steel extraction cartridge and extracted using 5% methanol (MeOH)/carbon dioxide (CO₂) (v/v) at 50° C and 6000 psi. Each sorbent was statically extracted for 30 minutes then dynamically for 0.5 -1.5 hours with collection of extracted material over 30 minute intervals during this time. Flowrates of the supercritical fluid were approximately 1 mL/min. Collection was in vials containing 2-3 mL of methylene chloride (MeCl₂). These solutions were then reduced to a final volume of approximately 1 mL with a N₂ flow.

Soxhlet conditions

Sorbent samples were weighed and placed in cleaned cellulose extraction thimbles. The thimbles were then loaded in the Soxhlet extractors and the extractors were charged with 200 mL of extraction solvent. 5% ether/hexane (v/v) was used for the Tenax-GC and Tenax-GR sorbents and MeCl₂ was used for XAD-2 and Carboxen 563. The Soxhlet extractors were then allowed to run for 16-18 hours; after which the solvent was rotary evaporated down to 3-4 mL and then transferred to an evaporation vial for final reduction to 1 mL with a N₂ flow.

Analysis by GC/MS

Once the samples were blown down to 1 mL, an internal standard of 4,4'-dibromo-1,1'-biphenyl was added at a concentration of 1 ng/μL. A 1-μL aliquot was then inject into a Hewlett-Packard GC/MS (HP5890/HP5971A, respectively) equipped with an XTI-5 column (Restek, Bellefonte, PA, 30 m, 0.25-mm i.d., 0.25-μm d.f., catalog # 12223).

Temporal and chemical stability

Once the sorbents were cleaned, the SFE cartridges were sealed and allowed to remain sealed for 4 weeks. This was done to determine if the sorbents remained clean once they were extracted. At the end of this 4-week period the sorbents were once again extracted by SFE as in the original clean up extraction above and the extract analyzed.

Chemical stability was investigated by exposing the sorbents to ozone and extracting them using SFE as above. The ozone exposure was 115 ppb for 18.5 hours at a flowrate of 1.3 L/min. with a relative humidity of 48-52% for the Tenax-GC and Tenax-GR. For the XAD-2 and Carboxen 563, ozone exposure was 115 ppb for 16.0 hours at 1.5 L/min. with a relative humidity of 40-50%. Again, the extracts were analyzed by GC/MS as above.

RESULTS

Initial "Clean-up" Extractions

As expected, analysis of the SFE and Soxhlet extracts from Tenax-GC, Tenax-GR, and Carboxen 563 revealed significant amounts of impurities in the first sequential extracts. However, the third sequential SFE extracts and the second sequential Soxhlet extracts showed no detectable impurity except a consistent phthalate ester component. This compound was found in all sorbents at varying levels but was greatly reduced with each subsequent extraction. It should be noted that it was much easier and quicker to reach this level of "cleanliness" using SFE (1.5-2 hours) than Soxhlet extraction (16-18 hours).

Analysis of the XAD-2 extracts revealed that this particular lot was surprisingly clean given past experience with XAD-2. Previously, XAD-2 was repeatedly extracted but still retained significant amounts of impurities. The impurities detected were the phthalate ester as

in the other sorbents and an acid ester. The acid ester was only observed in the Soxhlet extract. Subsequent extractions reduced the amount of these compounds in each extract.

During these initial clean-up extractions, it was noted that the hexane/ether mixture added significantly to the background signal. Therefore, higher purity hexane was purchased and the problem was eliminated.

The following observations were made after comparing the chromatograms of the sequential SFE and Soxhlet extracts for the various sorbents.

Tenax-GC

- There were four primary contaminants associated with this sorbent. Two were common to both the SFE and Soxhlet extracts and of the other two, one was found in each.

Tenax-GR

- There were ten primary contaminants and they were components of both the SFE and Soxhlet extracts at about the same relative levels.

XAD-2

- There were only two primary contaminants and one was associated with the SFE extract and the other was associated with the Soxhlet extract.

Carboxen 563

- There were nine primary contaminants and only one was associated with the SFE extract. The other eight were associated with the Soxhlet extract.

Temporal and Ozone Stability

Comments below pertain to chromatograms obtained from analysis of SFE extracts of sorbent sealed for 4 weeks then extracted (●) and sorbent exposed to ozone then extracted (○).

Tenax-GC

- Comparison of the third sequential extract before sealing and the first extraction after being sealed revealed that there was no residual contaminants except for the ever present phthalate ester mentioned above. Also, after a second extraction this peak also became negligible.
- Exposure to ozone did produce artifacts from the degradation of the Tenax-GC which could be problematic if ambient measurements of compounds such as benzaldehyde and acetophenone were being performed.

Tenax-GR

- Comparison of the third sequential extract before sealing and the first extraction after being sealed revealed that there was no residual contaminants except the phthalate ester. Again this was removed completely after the second extraction.

- Only two artifacts were formed from exposure to ozone and at levels lower than for Tenax-GC and did not include benzaldehyde nor acetophenone.

XAD-2 and Carboxen 563

- Comparison of the extracts before and after sealing showed no change in the sorbent.
- No effect on the sorbents was noted and no artifacts were extracted.

CONCLUSIONS

The following conclusions can be drawn from this preliminary study:

- ◇ Since the two extraction methods can extract different components from the sorbents, whichever method is used for clean up should also be used for the extraction of the sample collected on the sorbent.
- ◇ Tenax-GR is preferable to Tenax-GC because of its greater stability in O₃.
- ◇ XAD-2 and Carboxen 563 may be preferable to either Tenax type because of their ease of cleaning and stability in O₃. Comparison of their collection and recovery efficiencies to those of Tenax GC and GR will help determine this.
- ◇ For preparation of small amounts of sorbents such as sorbent cartridges, SFE would be preferable to Soxhlet extraction in terms of time and handling ease. A cartridge could be filled, cleaned, used, extracted, and possibly reused, all without having to remove and handle the sorbent thus minimizing the chance of contamination and sample loss.

DISCLAIMER

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