



Project Summary

Evaluation of an Anion Exchange Resin for Sampling Ambient Level Phenolic Compounds

Marcia Nishioka and Hazel Burkholder

The determination of human exposure to polar volatile and semivolatile organic compounds is an area of increasing importance to EPA. Since the bioavailability of many polar compounds is greater than for relatively non-polar compounds, methods are needed for the selective sampling and analysis of these types of compounds. The sorbent sampler described in this report provides a new capability of sampling for acidic and phenolic vapor phase organic compounds.

The currently available method for collection of vapor phase phenol and methyl-phenols, as described in EPA's Ambient Air Method TO-8, involves aqueous sodium hydroxide impinger collection. Solution sampling is, in general, not practical for field sampling at remote sites; in addition, this impinger method has not been evaluated for collection of chemically diverse and more toxic phenolic species such as the chloro- and nitro-phenols nor has it been shown sensitive enough for determinations at trace ambient levels. Based upon these considerations, the alternative method developed here utilizing solid sorbent based sampling may prove preferable to liquid based impinger methods.

The program described here was designed for evaluation of a solid sorbent, the anion exchange resin AG MP-1, for selective collection and retention of vapor phase phenolic compounds. The primary goal of the program was development of sampling and analysis conditions which would permit detec-

tion and quantification of diverse phenolic and hydroxylated species at ambient levels of 1 ppbv. Phenols (and other acidic compounds) are retained on AG MP-1 by formation of a chemical bond; the reaction is reversed to liberate the phenols from the sorbent prior to analysis. Because of the dominant concern about collection and recovery, investigations here centered upon those parameters which affect the formation of the initial chemical bond between phenolic analyte and sorbent and those procedures that allow subsequent reversal of these reactions for quantitative recovery of analytes.

Average recoveries of 89% (82-101%) were measured for 1 µg quantities of 13 chemically-diverse phenolic compounds that were spiked into a heated gas stream, sampled at 100 mL/min through AG MP-1, extracted from the AG MP-1, and concentrated prior to analysis. Recovery of a solution spike of these analytes to AG MP-1 without subsequent gas sampling averaged 85% (76-104%). Because recoveries from the two spiking experiments were comparable, it was concluded that vapor phase collection was essentially quantitative.

This Project Summary was prepared by the EPA's Atmospheric Research and Exposure Assessment 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 currently available method for collection of vapor phase phenol and methylphenols involves aqueous sodium hydroxide impinger collection. Solution sampling is, in general, not practical for field sampling at remote sites; in addition, this impinger method has not been evaluated for collection of chemically diverse and more toxic phenolic species such as the chloro- and nitro-phenols. Sorbent based sampling methods are preferable to impinger methods. As an alternative to the impinger method, PUF (polyurethane foam)-Tenax-PUF sandwich sorbent cartridges have been evaluated recently for the collection of vapor phase chloro-phenols. While this method provides high collection efficiencies for the tetra- and pentachlorophenols, mono-chloro-phenols are not retained. These collection differences suggest that phenol and mono-functional phenols (e.g. methylphenols, nitro-phenols) also will not be retained by this sorbent.

The program described here was designed for evaluation of a solid sorbent, the anion exchange resin AG MP-1, for selective collection and retention of vapor phase phenolic compounds. The primary goal of the program was development of sampling and analysis conditions which would permit detection and quantification of diverse phenolic and hydroxylated species at ambient levels of 1 ppbv. The program also included 1) the development of methods for removing potential neutral interference compounds which could be retained by adsorption to the sorbent polymer backbone, 2) evaluation of stability of sorbent-bound analytes during prolonged storage, and 3) stability of sorbent-bound analytes toward nitration by ambient HNO_3 . In addition, the program included preliminary field sampling evaluation of the sorbent. Field collection was carried out at two sites in northern Delaware; three additional samples were collected in the Columbus, Ohio area.

Anion exchange resins/sorbents are typically suspended in aqueous or organic media for chromatographic separations. For the strongly basic anion exchange resins, such as AG MP-1, the charge is fixed by the structure of the resin; positively charged quaternary amine groups are chemically bound to a styrene divinylbenzene lattice; the negatively charged counterion to the amine can be exchanged. The quaternary amine retains its charge whether or not the resin is suspended in solution. AG MP-1, available from Bio-Rad Laboratories, is a macroporous strong anion exchange resin. Because of the highly crosslinked and relatively rigid styrene divinylbenzene backbone, AG MP-1 does not shrink or swell

excessively during extraction of analytes with solvents and is not crushed easily during sampling and handling. The high degree of porosity allows retention of larger, less polar organic acids and phenols so as to increase contact time for formation of the chemical bond between analyte and quaternary amine. AG MP-1 is similar to the XAD-2 resins in physical properties such as ease of handling, mechanical strength, and color.

For sorbent sampling based upon adsorption, as with XAD-2, collection and retention are both described by chromatographic theory, the dominant factor being partition of analyte between gas and solid phase. For the anion exchange resin evaluated here, collection and retention are two separate issues. Phenols (and other acidic compounds) are retained on AG MP-1 by formation of a chemical bond; the reaction is reversed to liberate the phenols from the sorbent prior to analysis. Schematic representation of these steps is shown in Figure 1.

Experimental

For experiments conducted on this program, AG MP-1 was converted from the manufacturer-supplied Cl^- form to the OH^- form to obtain the strongest possible aqueous base (OH^-) for exchange. The OH^- on the resin will readily abstract a proton from phenolic and acidic organic analytes and thus effect attachment of an analyte anion to the quaternary amine exchange site. Analyte anions are displaced from the resin later by application of an acid of greater strength than the analytes, in this case 2% conc. HCl in 15:85 (v:v) methanol:methyl-t-butyl ether. Under these conditions the Cl^- form of the resin is generated and the organic analyte is regenerated as a neutral molecule. Because formation of the chemical bond ensures retention of analytes, retention is the lesser important of the two considerations. Phenols will be retained unless sampling occurs in atmospheres of very high HNO_3 concentrations (or other acid whose pK_a is less than that of the phenols of interest) where HNO_3 may either displace phenols from the sorbent or nitrate the phenols and, thus, form artifacts. Because of the dominant concern about collection, investigations here have centered upon those parameters which affect the formation of the initial chemical bond between phenolic analyte and sorbent.

The target level for phenols in these laboratory experiments was 1 μg for each analyte. The 1 μg level represents the average quantity for phenols which, if present at 1 ppbv in the atmosphere, would be collected during a 24 hr period when sampling at 100 mL/min with 100% collection

efficiency at ambient temperature and pressure. For phenols of interest, the quantity collected covers a range from 0.5 μg for phenol to 1.5 μg for pentachlorophenol. The target level for analysis in these laboratory experiments has been 1 ng/ μL . This quantification level is required for the analysis of the 1 μg spike quantities when fully recovered and concentrated to a 1 mL volume.

After collection and prior to analysis, phenols are subjected to two extraction procedures: extraction from AG MP-1 with an acidified solvent (HCl in methanol/methyl-t-butyl ether) and then extraction from that acidified sorbent eluate into a neutral solvent. The experimental plan for the program involved, in sequence: (1) development and evaluation of GC and GC/MS analysis conditions; (2) evaluation of methods to extract phenols from acidified sorbent eluate; (3) evaluation of methods to extract phenols (and neutral compounds) from sorbent; (4) evaluation of parameters which affect collection of vapor phase phenols, and finally; (5) analysis of field-collected samples.

The following experimental procedures for (both laboratory and field work) were developed in this program:

- Preparation and storage of standard analyte mixtures
- Activation and storage of resin
- Analysis methods
 - a. GC/FID for laboratory tests at high levels
 - b. GC/ECD for laboratory tests for low levels of nitro- and chloro-phenols
 - c. GC/FID for neutral interference compounds
 - d. GC/MS for field collected samples
- Extraction of phenols from acidic methanol:methyl-t-butyl ether
- Extraction of phenols from AG MP-1
- Extraction of neutral interference compounds from AG MP-1
- Method for vapor spike and simulated sampling of phenols
- Method for evaluating stability of sorbent bound phenols
 - a. Stability during one-month storage
 - b. Stability toward HNO_3
- Collection of field samples
 - a. preparation of sorbent tubes
 - b. collection of field samples
 - c. extraction and analysis

The many and varied exploratory experiments performed to develop this new methodology cannot be discussed in detail in this summary; procedures are presented in detail in the complete report.

Retention and Elution of Phenols from AG MP-1

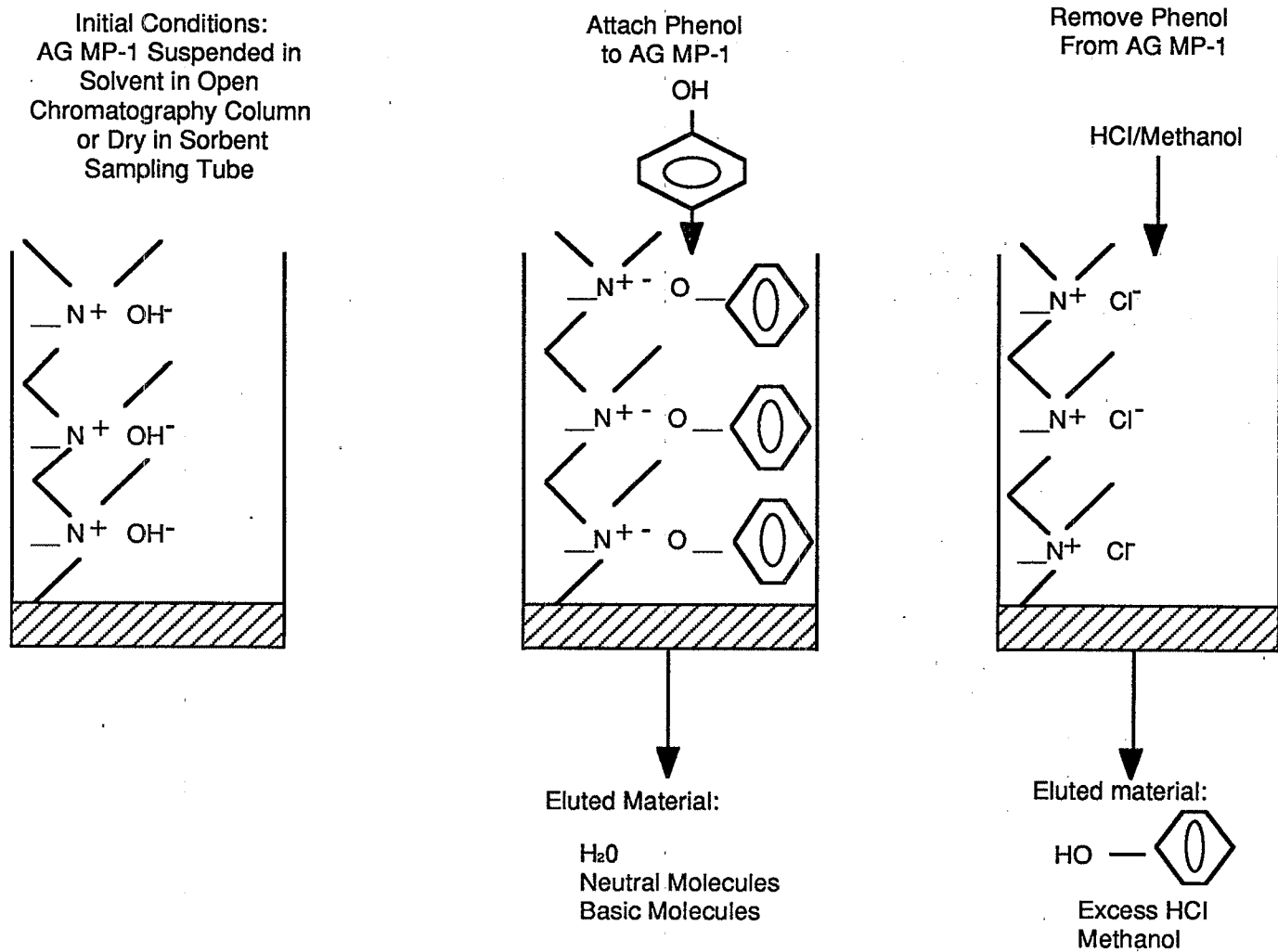


Figure 1. Schematic representation of collection of phenols with AG MP-1 and subsequent elution.

Results and Discussions

Detailed presentations of results and relevant discussion are given in the full report for each laboratory and field experiment. For this summary, only highlights are presented for selected collection/recovery experiments; these are representative of the overall effort.

The parameter tests resulted in a nominally optimized procedure for sampling vapor phase phenolic compounds and subsequently extracting them quantitatively. This is a laboratory experiment performed under the best conditions using a clean helium carrier gas. To control for any matrix effects during subsequent experiments with ambient air matrices, this method was used for pre-spiking sorbent tubes with deuterated phenolic compounds to further test recoveries. The optimized configuration of mesh size (200-400), flow rate (100 ml/min), and linear velocity (1.75 cm/sec) resulted in the recovery data presented in Table 1 for 13 phenolic compounds representing phenol and methyl phenols, chlorophenols, nitrophenols and related compounds.

Table 2 presents recovery data for deuterated compounds after real field sampling, both for compounds spiked prior to field sampling and for laboratory recovery standards. These representative results indicate that overall recoveries are more scattered than for the laboratory tests and that some of this scatter could be caused by the laboratory recovery procedure.

Based upon results from all of the laboratory tests, sorbent mesh size and superficial linear sampling velocity were those parameters which affected collection efficiency most dramatically. Sampling was most efficient with the 200-400 mesh AG MP-1 (particle diameter range of 38-75 μm) at a linear velocity of 1.75 cm/sec. Field-collected samples showed that neutral species such as aliphatic and aromatic hydrocarbons were retained by this sorbent in addition to the phenolic and acidic species. For this reason, extraction methods were developed for selective extraction of neutral species prior to extraction of phenols. These methods were developed for neutral species levels 1000 times greater than anticipated phenol levels and resulted in greater than 90% recovery of spiked neutral species.

Recommendations

Based on the results of this study, sampling at 100 mL/min for vapor phase phenols may be applied best to air heavily impacted by specific emission/pollution sources. The method evaluated here may not provide sufficient sensitivity for ambient levels less than 1 ppbv. Therefore, the recommendations listed here are divided into two categories, those specific to the further evaluation and development of the sorbent sampler described here and those specific to development of a similar AG MP-1 based sampler compatible with higher sampling rates. It is recommended that further study of the following areas be performed:

Existing Method:

- Evaluation of the retention of vapor phase phenols by acid-washed glass fiber and quartz fiber filters.
- Evaluation of the components of laboratory AG MP-1 method blanks, with particular emphasis on phenolic and acidic species.
- Evaluation of extraction procedures which ensure complete recovery of phenolic/acidic analytes following extended (12-24 hr) sampling periods at 100 mL/min.
- Evaluation of the collection efficiency of AG MP-1 sorbent for phenols from very dilute gas streams.
- Further evaluation of stability of phenols and extraction efficiency from AG MP-1 following storage.
- Further evaluation of stability of phenols toward ambient levels of nitrating gases.

New Sampler (higher sampling rates):

- Development of an AG MP-1 based sorbent sampler for operation at 1-2 L/min and at 10-100 L/min to increase sensitivity.
- Development of an AG MP-1 based passive sampler with nominal sampling rate of 80-100 mL/min for fast sampling without electrical requirements.
- Evaluation of the anion exchange membrane AG 1-X8 (available from Bio-Rad; 90% AG 1, chemically similar

Table 1. Recovery of Phenols after Vapor Spike: 200-400 Mesh AG MP-1; 1 μg Phenol 100 mL/min Sampling Rate; 11 mm I.D. Sorbent Tube.

Analyte	% Recovery	(% DM)(a)
Phenol	91	1
2-CH ₃ -phenol	87	1
4-CH ₃ -phenol	92	8
2,3-diCH ₃ -phenol	82	2
2-Cl-phenol	85	5
4-Cl-phenol	89	2
2,4-diCl-phenol	92	2
PentaCl-phenol	82	(b)
2-NO ₂ -phenol	82	(b)
3-NO ₂ -phenol	99	5
6-CH ₃ -2-NO ₂ -phenol	92	2
2-OH-benzaldehyde	101	7
2-OH-biphenyl	86	2

(a) $n = 2$; % deviation from the mean.

(b) Single analysis; analyte recoveries were 33% and 6% in 2nd sorbent extract for 2-NO₂-phenol and pentaCl-phenol, respectively.

Table 2. Recovery of Deuterated Compounds from Columbus, Ohio Collected Samples.

Sample Designation	% Recovery					
	Field Recovery Standard 20 µg			Lab Recovery Standard 5 µg		
	Phenol- <u>d</u> ₆	4-NO ₂ - <u>phenol-d</u> ₄	2,4-diCl- <u>phenol-d</u> ₃	4-CH ₃ - <u>phenol-d</u> ₅	2-NO ₂ - <u>phenol-d</u> ₄	2-Cl- <u>phenol-d</u> ₄
Municipal Bus Garage	103	80	100	108	120	106
Municipal Compost Facility	98	39	68	104	42	91
Lab Blank	69	47	89	90	66	62

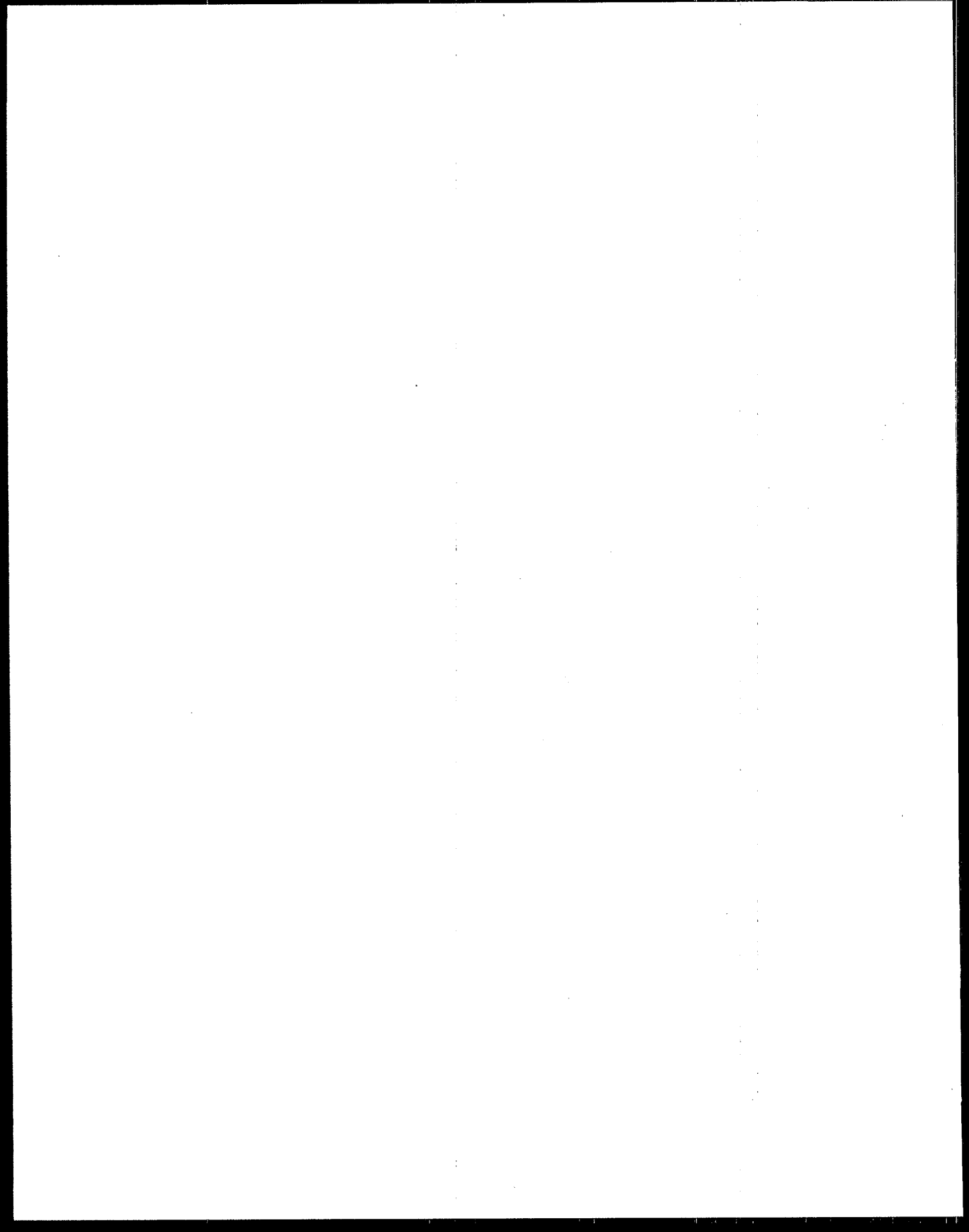
to AG MP-1, incorporated into a polytetrafluoroethylene matrix) as an inlet filter on canisters or Tenax samplers.

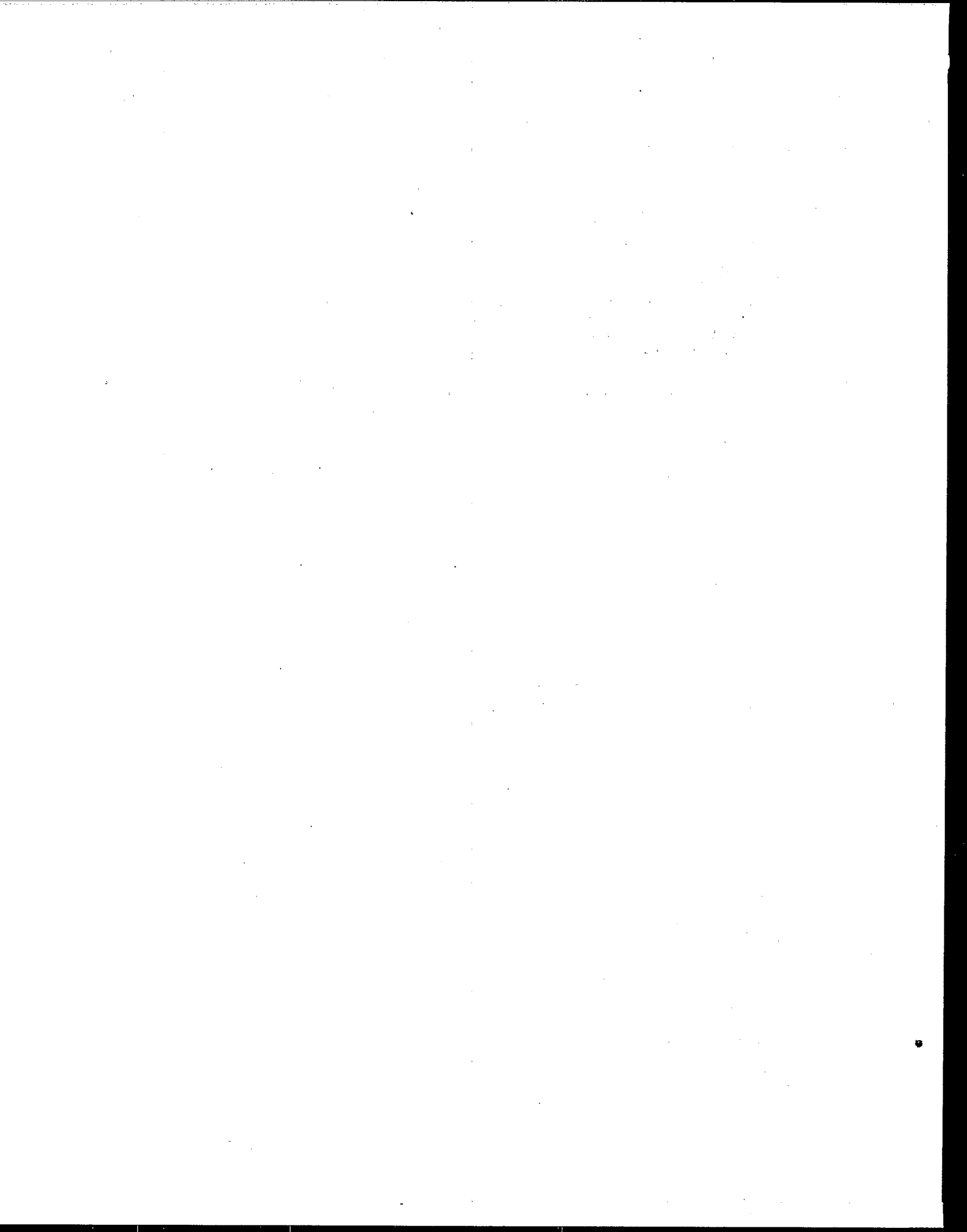
- Evaluation of the anion exchange membrane AG 1-X8 as the inner surface of an annular denuder sampling system for determining phase distribution for the less volatile phenolic compounds.

Conclusions

The newly developed method for the determination of ambient phenolic compounds was successfully optimized and laboratory tested. Representative compounds exhibit an average collection/recovery of 89% for 1µg quantities sampled at 100 ml/min through the anion exchange sorbent AG MP-1. The method is a viable

approach for trace-level determination of ambient phenolic compounds. Parameter testing and use of deuterated recovery standards indicate that further work is necessary to optimize sensitivity via sampler development (sorbent tube and pump-systems), and to further develop and optimize laboratory extraction procedures.





Marcia Nishioka and Hazel Burkholder are with Battelle Columbus Laboratories, Columbus, OH 43201.

Joachim D. Piell is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of an Anion Exchange Resin for Sampling Ambient Level Phenolic Compounds," (Order no. PB90 246 091AS; Cost:

\$23.00 cost subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Atmospheric Research and Exposure Assessment Laboratory

U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/S3-90/055

• •

• •