Journal of Chromatography, 393 (1987) 367–376
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 415

EVALUATION OF POROUS POLYMER TRAPS FOR ANALYSIS OF FOUR VOLATILE N-NITROSAMINES USING THERMAL DESORPTION INJECTION COUPLED WITH A GAS CHROMATOGRAPH–THERMAL ENERGY ANALYZER

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(First received September 22nd, 1986; revised manuscript received January 9th, 1987)

SUMMARY

Three porous polymer adsorbents, Tenax-TA, Chromosorb 102, and Chromosorb 103 were investigated as potential gas phase, trapping agents for volatile N-nitrosamines using a thermal desorption injector coupled with a gas chromatograph–thermal energy analyzer. N-Nitrosodimethylamine was used as the model N-nitrosamine for determining break-through volume, the effect of temperature on retention volume, and collection efficiency at 25°C for each adsorbent.

Results from these three parameters indicated that Chromosorb 103 exhibited the best adsorbent characteristics for the pre-concentration of volatile N-nitrosamines. A mixture of three dialkyl N-nitrosamines (dimethyl, diethyl, and dipropyl), and N-nitrosopyrrolidine were analyzed using a high-temperature mineral oil purge and trap procedure. Recoveries ranged from 82.2 to 102.8% at levels of 10 and 100 ng of each N-nitrosamine added.

INTRODUCTION

Tenax-GC™, a porous polymer of 2,6-diphenyl-*p*-phenylene oxide, has been used extensively as a vapor trapping adsorbent for the gas chromatographic (GC) analysis of many hazardous organic pollutants[1–4]. Most of the work involving N-nitrosamines has been in the analysis of N-nitrosamine levels in air samples[1,5–7]. Rounbehler *et al.*[6] evaluated a series of traps including Tenax-GC, dry adsorbents (charcoal, alumina, silica gel and Florisil), wet impinger traps (1 *M* potassium hydroxide and pH 4.5 phosphate–citrate buffer 20 mM ascorbic acid), and ThermoSorb/N™ (a mixture of metal silicates, amine trapping agents, and antioxidants) for analysis of seven volatile N-nitrosamines in air. Their results showed the ThermoSorb/N cartridges to be superior in recovery of N-nitrosodimethylamine (NDMA) and in freedom from artifact formation over Tenax-GC and the other traps tested.

A more recent study using the ThermoSorb/N cartridge utilizing a high-temperature mineral oil purge method and gas chromatography–thermal energy analysis (GC–TEA) has been reported for analysis of volatile N-nitrosamines in cooked ba-

con[8] and animal feed[9]. These methods have exhibited excellent recoveries with a minimum of analytical steps and are extremely time and cost efficient. However, the ThermoSorb/N cartridge must be eluted with acetone or acetone–dichloromethane (1:1) before injection into the gas chromatograph–thermal energy analyzer. Therefore, the concentration effect of the N-nitrosamine on the cartridge has been negated by dilution of the sample limiting the detection limits of the method. The sensitivity of the mineral oil purge method could be greatly enhanced using a porous polymer trap which can be analyzed by a thermal desorption injector coupled to a gas chromatograph–thermal energy analyzer.

This paper presents an evaluation of several porous polymers, Tenax-TA™, Chromosorb 102™ (a styrene–divinylbenzene polymer), and Chromosorb 103™ (a cross-linked polystyrene polymer) as possible N-nitrosamine trapping agents for the mineral oil purge method. NDMA, the most volatile and most difficult of the N-nitrosamines to trap was used as a model for comparing the polymer adsorbents break-through volume, effect of temperature on retention volume, and collection efficiency at ambient temperature. Recoveries of NDMA, N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), and N-nitrosopyrrolidine (NPYR) are determined from mineral oil spiked with 10 and 100 ng each using a Chromosorb 103 trap. A sensitivity comparison is made between GC–TEA analysis using the ThermoSorb/N cartridge *versus* the thermal desorption injection (TDI)–GC–TEA procedure.

EXPERIMENTAL

Materials

Standard stock solutions of NDMA, NDEA, NDPA and NPYR (Eastman, Rochester, NY, U.S.A.) were prepared by diluting 100 mg of each compound to 50 ml with ethanol. The analytical standards were prepared by making appropriate dilutions of the stock solutions in dichloromethane (Burdick and Jackson, Muskegon, MI, U.S.A.). A standard containing 2 μg/μl of NDMA in dichloromethane was used in the study of break-through volume of the adsorbents. The NDMA standard used for determining retention volumes contained 100 ng/μl in dichloromethane. Standard solutions used for determining recoveries from the mineral oil purge method contained 1 ng/μl and 10 ng/μl, of NDMA, NDEA, NDPA and NPYR in dichloromethane. Caution: volatile N-nitrosamines are extremely hazardous compounds. All manipulations involving handling their neat liquids or solutions should be carried out in an adequately ventilated and filtered fume hood or glove box. The porous polymers, Tenax-TA (20–35 mesh) (a Tenax of larger particle size especially processed as a trapping agent for volatiles), Chromosorb 102 (20–40 mesh), and Chromosorb 103 (20–40 mesh) were supplied by Anspec, Ann Arbor, MI, U.S.A.

The sample collection traps were made of glass tubes (13 cm × 7 mm O.D. × 4 mm I.D.). The tubes were packed with pre-conditioned porous polymer and the packing was contained in the tubes by two 5-mm silanized glass wool plugs.

Porous polymer pre-conditioning procedure

As shown by Betti *et al.*[10], the pre-conditioning temperature for these porous polymers, especially the styrene based packings, was found to be extremely important

to the reproducibility of the adsorbent properties. The Chromosorb 102 and 103 were conditioned for 16 h at 225°C and 275°C, respectively, (25°C under their maximum operating temperature) with 40 ml/min argon gas flow, then for an additional hour at 250°C and 300°C, respectively. Tenax-TA was conditioned at 325°C for 16 h with 40 ml/min argon flow, then for an additional hour at 350°C. A slight darkening of the polymers may occur, but this does not adversely effect the adsorbent characteristics. After pre-conditioning, each packing was combined in separate glass scintillation vials and rotated gently to help homogenize and break up any clumps of polymer particles formed. Each homogeneous, pre-conditioned polymer was then added to account for the appropriate weight of adsorbent to the tubes previously described. Each finished trap was subjected to the stripping procedure before being used to remove any airborn contaminants collected during packing.

Stripping apparatus and procedure

Since porous polymers vary widely in their ease of thermal desorption, a stripping apparatus (Fig. 1) was designed similar to that reported previously[11] which strips the collected volatiles from one trap to another for subsequent analysis by TDI–GC–TEA. This process served dual purposes of (i) allowing each trap to be reproducibly loaded onto a second trap to eliminate differences in purge rate, sampling time, and adsorbent type which could effect the desorption pattern during TDI–GC–TEA analysis and (ii) acting as a secondary clean-up step following the mineral oil purge and trap procedure. The secondary trap was a tube containing 0.15 g of Tenax-TA (20–35 mesh) conditioned as described. Tenax-TA was chosen due to its quick release of volatiles and its high temperature stability (400°C) which allowed it to be programmed quickly to 350°C without appreciable bleed or polymer degradation.

The stripping procedure was initiated by assembling the apparatus as shown in Fig. 1. The stripping conditions were standardized at a 300°C tube heater temperature with a 100 ml/min argon flow for 10 min sampling time period. The trap containing the stripped sample was capped and stored in the dark at room temperature until TDI–GC–TEA analysis. The other trap was removed from the heated zone and allowed to cool to room temperature with argon gas flow before disconnecting. This stripping procedure allowed for a quantitative transfer of all N-nitrosamines tested using each type and amount of porous polymer studied.

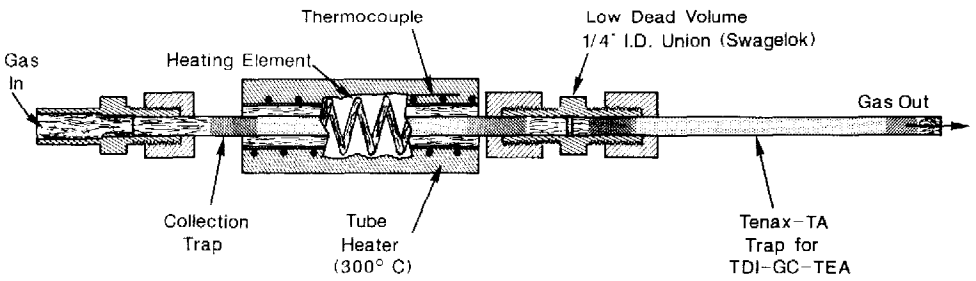

Fig. 1. Stripping apparatus for the transfer of volatile N-nitrosamines to a Tenax-TA trap for TDI–GC–TEA analysis.

TDI–GC–TEA system

The thermal desorption injector, similar to those described previously[2,11] is shown in Fig. 2. The injection port of a Hewlett-Packard Model 5710A gas chromatograph was modified by connecting the injector directly into its carrier gas line. This arrangement allowed for routine solvent GC injections and in addition allowed for gas phase injections via the thermal desorption injector. A high temperature four-port valve (Valco, Houston, TX, U.S.A.) connected to an aluminum block operated at 200°C, was used to divert the carrier gas to the GC column while the adsorbent trap was positioned in the thermal desorption injector for analysis. The thermal desorption injection was initiated by rotating the valve handle manually 90° to the left connecting the trap to carrier gas (40 ml/min argon) which flowed into a 50°C analytical column. The thermal desorption injector tube heater was ballistically heated to 350°C in 1 min and held for an additional 2.5 min. The injection was then terminated by rotating the valve 90° to the right. The tube heater was allowed to cool to room temperature before removing and capping the trap.

The analytical GC column was a 1.8 m × 4 mm I.D. glass column packed with 10% Carbowax 20M–2% KOH on 80–100 mesh Chromosorb WAW (Supelco, Bellefonte, PA, U.S.A.) conditioned at 215°C overnight prior to use. The column was operated with a 1-min initial hold time at 50°C then programmed at a rate of 16°C/min to a final temperature of 190°C with a 40 ml/min pre-purified argon carrier flow. The GC injection port temperature was set at 250°C.

The GC column was interfaced to a Thermal Energy Analyzer™ Model 502 updated with a 610R nitrogen converter (Thermedics, Waltham, MA, U.S.A.). The pyrolysis chamber of the thermal energy analyzer was operated at 500°C in the nitroso mode. The oxygen flow to the ozonator was 10 ml/min. A CTR™ gas stream filter (Thermedics) was used in place of the cryogenic trap previously[9] used for trapping out pyrolysis by-products. The pressure of the reaction chamber was 0.9 Torr.

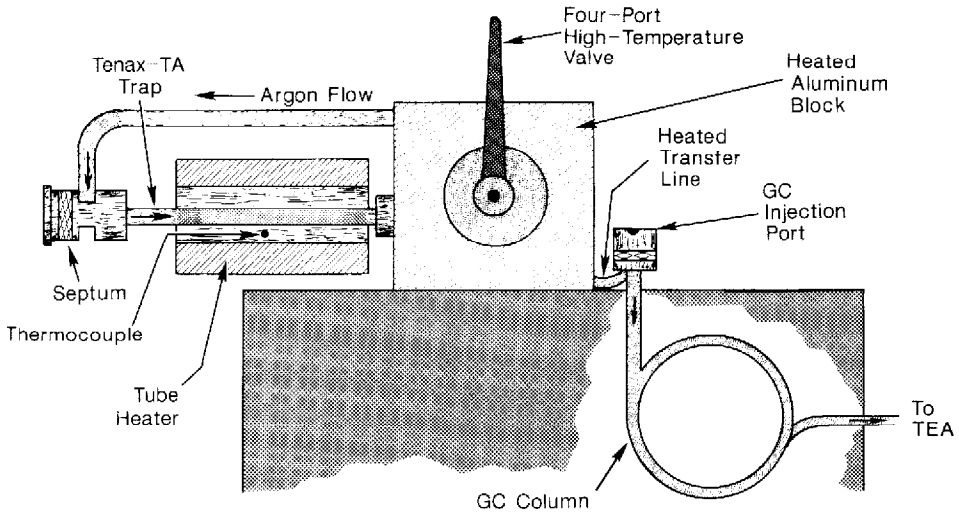

Fig. 2. Diagram of the thermal desorption injector coupled to a gas chromatograph–thermal energy analyzer.

The response of the thermal energy analyzer was recorded on a Spectra Physics SP-4100 integrator which was activated at 7.5 min after the start of the thermal desorption injection which allowed ample time for restabilization of GC–TEA response before collecting data.

Mineral oil purge apparatus

The mineral oil purge apparatus and its operation has been previously described[9]. Basically, four 50-ml impinger tubes are connected via ground-glass ball joints to a variable flow gas purge manifold. A high-temperature oil bath is used to isothermally heat the impinger tubes during purging. The adsorbent trap is connected to the outlet of the impinger tube with Tygon™ tubing connectors.

Recovery experiment with the mineral oil purge and trap method

A volume of 20 ml of mineral oil and 0.5 g of sulfamic acid (nitrosation inhibitor) was added to a 50-ml impinger tube. The mineral oil was spiked with the N-nitrosamine test mixture and swirled to mix. A small silanized glass wool plug (approx. 0.05 g) is inserted just before the trap to prevent contamination of the adsorbent by mineral droplets formed during purge. The impinger was then assembled with a Chromosorb 103 trap (0.3 g) to collect the purged volatiles. The oil bath is raised into position with a lab jack to the 25-ml mark on the impinger tube and the N-nitrosamines are volatilized by purging with 0.4 l/min argon for 1 h at a 150°C oil bath temperature. The adsorbent trap is capped and subjected to TDI–GC–TEA analysis.

RESULTS AND DISCUSSION

Determination of break-through volumes

Break-through volumes (BTVs) were determined for all three porous polymers (see Table I) by using the procedure of Kashihira *et al.*[4]. The specificity of the TEA detector to the appearance of compounds containing N-nitroso groups (N–N=O) was determined by detecting a rise in baseline following injection of 2 μg of NDMA directly into the tube containing adsorbent. Fig. 3 illustrates a typical break-through curve showing an increase in the TEA response at the time NDMA began breaking through the adsorbent barrier. The volume of gas (l) was calculated by extrapolating the break-through time from the curve and multiplying by the fixed flow-rate (0.05

TABLE I

LIST OF POROUS POLYMERS TESTED AND THEIR PHYSICAL AND CHEMICAL PROPERTIES

Adsorbent	*Type*	*Surface area (m^2/g)*	*Density (g/ml)*	*Average pore size (μm)*	*Mesh*	*Maximum operating temperature (°C)*
Tenax-TA	2,6-Diphenyl-*p*-phenylene oxide	35	0.16	0.200	20–35	400
Chromosorb 102	Styrene–divinyl benzene	300–400	0.34	0.0085	20–40	250
Chromosorb 103	Polystyrene	15–25	0.37	0.3–0.4	20–40	300

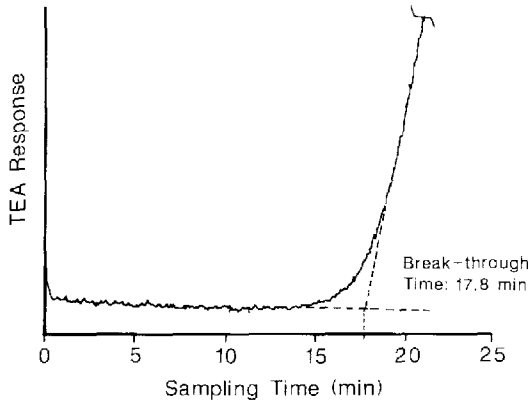

Fig. 3. Break-through curve for NDMA using Tenax-TA (0.05 g) trap.

l/min). The BTVs at 25°C for each polymer are reported in Table II in l and l/g of polymer. Chromosorb 103 with a 29.9 l/g BTV exhibited a significantly higher capacity for retaining NDMA than the other adsorbents. Tenax-TA with approximately one-half the density (Table I) of Chromosorb 102 and Chromosorb 103 exhibited poor efficiency and had the disadvantage of a lower weight of polymer per packed volume in a collection tube. Chromosorb 102 was shown to have a surprisingly low BTV especially since its adsorbent surface area (300–400 m^2/g) is 10-fold greater than that of Tenax-TA and Chromosorb 103. The low BTV was attributed to the chemical structures of Chromosorb 103 and Tenax-TA having a greater affinity for the N-nitroso group than Chromosorb 102, thus overcoming the higher surface area of the latter.

Effect of temperature on retention volume of an adsorbent

Another technique used frequently for comparing the trapping ability of an adsorbent is to study the retention volume (volume of gas required at a fixed flow-rate to elute the peak maxima of the component injected) *versus* variation in temperature. This method was investigated by connecting the tube containing the polymer (0.30 g for Chromosorb 102 and Chromosorb 103 and 0.15 g for Tenax-TA) to the injection port of the gas chromatograph and the TEA detector via a low-dead

TABLE II

BREAK-THROUGH VOLUMES (BTVs) OF POROUS POLYMERS AT 25°C FOR NDMA

All BTVs were determined in duplicate using 2 μg total NDMA injected with a constant flow-rate of 0.05 l/min argon gas.

Adsorbent	*Weight of adsorbent (g)*	*BTV (l)*	*BTV (l/g)*
Tenax-TA	0.050	0.96	19.3
Chromosorb 102	0.100	0.72	7.2
Chromosorb 103	0.080	2.39	29.9

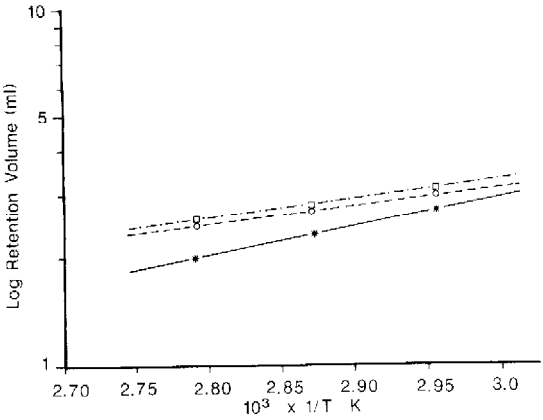

Fig. 4. Linear plot of log retention volume of NDMA *versus* 10^3 × reciprocal K for (*) Tenax-TA, (○) Chromosorb 102 and (□) Chromosorb 103.

volume connector. The sample (5 μl) of 100 ng/μl NDMA in dichloromethane was introduced directly into the GC injection port. The flow-rate was kept constant at 100 ml/min. Retention volume was calculated for each polymer at 65, 75 and 85°C. A linear relationship is shown in Fig. 4 for a plot of log retention volume *versus* $10^3 \times 1/T$ K for Tenax-TA, Chromosorb 102, and Chromosorb 103 exhibited higher retention volumes at all three temperatures indicating superior retention of NDMA over the other adsorbents tested. An attempt at extrapolation of these plots to 25°C (or 3.36 reciprocal K) did not agree well with the results of the BTVs determined. Evidently, a deviation from linearity at lower temperature is observed similar to that reported by other researchers[12,13].

Comparison of collection efficiency of adsorbent traps at various flow-rates

Ultimately, the NDMA collection efficiency for the various porous polymers at room temperature (25°C) is needed to demonstrate their utility as trapping media. In order to cover a wide range of possible purge rates, collection efficiency was determined for a 2-h trapping time at 0.1, 0.2 and 0.4 l/min (or 12, 24 and 48 l total gas volume, respectively). The results of this study are reported in Table III. After purg-

TABLE III

COLLECTION EFFICIENCY OF NDMA ON POROUS POLYMERS AT VARIOUS FLOW-RATES AT 25°C

Amount of NDMA added was 5 μl of 100 ng/μl in dichloromethane, purged directly onto the adsorbent trap at the flow-rate indicated for 2 h and analyzed by TDI–GC–TEA.

Adsorbent	*Weight of adsorbent (g)*	*Collection efficiency (%)*		
		0.1 l/min	*0.2 l/min*	*0.4 l/min*
Tenax-TA	0.15	81.1	41.9	10.5
Chromsorob 102	0.30	97.2	83.6	65.4
Chromosorb 103	0.30	100	96.3	71.0

TABLE IV

RECOVERY (%) OF FOUR VOLATILE N-NITROSAMINES FROM MINERAL OIL USING THE CHROMOSORB 103

Triplicate TDI–GC–TEA assays were performed at each spike level from mineral oil purged at 0.4 l/min argon flow and 150°C oil bath temperature for 1 h. The Chromosorb 103 traps contained 0.3 g of adsorbent conditioned at 275°C overnight and 300°C for 1 h at 40 ml/min. ND = none detected (*i.e.* less than the reported MDL).

Spike level (ng)	*% Recovery ($\bar{x}$ ± S.D.) of N-Nitrosamine*			
	NDMA	*NDEA*	*NDPA*	*NPYR*
0	ND	ND	ND	ND
10	94.6 ± 1.2	97.6 ± 1.7	94.5 ± 4.3	82.2 ± 1.2
100	96.3 ± 0.2	102.8 ± 0.9	99.4 ± 0.6	88.9 ± 2.0
MDL (ng)	0.22	0.28	0.30	0.46

ing with 48 l of argon gas, the Chromosorb 103 and Chromosorb 102 traps contained 71.0 and 65.4%, respectively, of the NDMA added with only 10.5% being retained by the Tenax-TA.

Recovery of a mixture of N-nitrosamines from mineral oil purge and trap apparatus using Chromosorb 103

In Table IV, the recoveries from mineral oil are reported for triplicate TDI–GC–TEA assays at 0-, 10- and 100-ng spike levels of a N-nitrosamine mixture containing NDMA, NDEA, NDPA and NPYR oil. The mineral oil was purged for 1 h at a purge rate of 0.4 l/min and an oil bath temperature of 150°C. These experimental conditions were used due to the optimum conditions reported previously[9]. The results for this method indicated excellent recovery and standard deviation for all N-nitrosamines tested ranging from 88.9 ± 2.0 to 102.8% ± 0.9% for the 100-

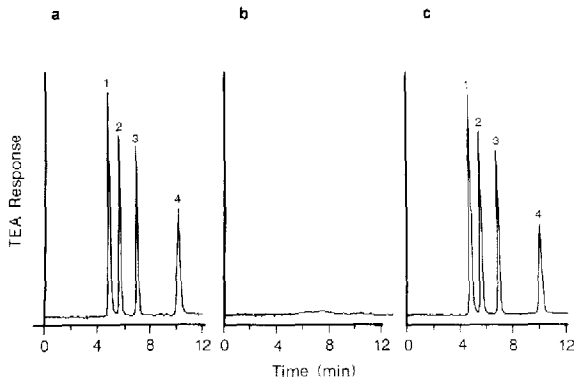

Fig. 5. Typical TDI–GC–TEA analyses. (a) 10-ng standard N-nitrosamine mixture of NDMA (1), NDEA (2), NDPA (3) and NPYR (4); (b) Tenax-TA trap blank (no N-nitrosamines added); and (c) 10-ng spiked mineral oil after purging at 0.4 l/min and 150°C for 1 h and trapping on a Chromosorb 103 (0.3 g) trap.

ng spike level and 82.2 ± 1.2 to 97.6% ± 1.7% for the 10-ng level. The choice of NDMA, NDEA and NPYR was made with the idea of screening for most of those N-nitrosamines having been reported in various food[14] and animal feed[9,15] products since 1970. Although it has never been reported as a contaminant in any product for human or animal consumption, NDPA was included since it is an excellent candidate for use as an internal standard in analysis of these products.

Comparison of sensitivities of the ThermoSorb/N and TDI–GC–TEA methods

The sensitivities previously reported[9] for the ThermoSorb/N method ranged from 3.0 to 11.1 ng for NDMA and NPYR, respectively. These minimum detectable levels (MDLs) were based on an 8-μl injection of 2-ml elution volume collected from the cartridge. Chromatograms using the TDI–GC–TEA method are shown in Fig. 5 for (a) a 10-ng standard mixture, (b) a blank Tenax-TA trap, and (c) a 10-ng spiked mineral oil. Based on these typical TEA responses, MDLs ranged from 0.2 to 0.5 ng for NDMA and NPYR, respectively, for the TDI method or approximately a 20-fold increase in sensitivity over the solvent injection method.

CONCLUSIONS

From this study, it was evident that BTV values alone could lead to erroneous conclusions concerning the usefulness of an adsorbent for trapping a specific component. Contrary to the BTV values determined, the retention volume and collection efficiency of Chromosorb 102 indicated that its effectiveness of retaining NDMA is quite comparable to Chromosorb 103 and much greater than Tenax-TA. Although a Chromosorb 103 trap was used for the mineral oil recoveries, Chromosorb 102 should also give similar results and possibly several other porous polymers not tested here. However, the evaluation of these few porous polymers has proven the feasibility of trapping volatile N-nitrosamines using a high-temperature purge and trap method. With the trend of analytical methods being directed toward less costly automated methods. Purge and trap methods of this type using cheap, re-usable polymer traps can be easily automated by use of programmable TDI instruments available on the market.

This method should be applicable to a wide variety of N-nitrosamine containing food or feed related products. However, it must be noted that most of the products containing N-nitrosamine contaminants also contain nitrite and/or nitrate salts and free amine precursors of the particular N-nitrosamine(s) found. Therefore, as we discussed previously[9], it is imperative that artifact formation tests be conducted for each type of product analyzed by this method. Presently, the method is being tested for the analysis of trace levels of NDMA and NPYR in laboratory animal feed.

ACKNOWLEDGEMENT

The authors would like to thank Patricia Norris for typing the manuscript.

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