Determination of Volatile Nitrosamine Contaminants in Formulated and Technical Products of Dinitroaniline Herbicides

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Routine methods for the measurement of volatile nitrosamines in several dinitroaniline herbicide products are described. Samples are dissolved in or extracted with an appropriate solvent and the nitrosamines are separated from the herbicides by alumina column chromatography. Eluate fractions containing nitrosamines are concentrated and the nitrosamines are measured using a gas chromatography–thermal energy analyzer system. Nitrosamines can be readily determined at the 0.1-ppm level.

Ross et al. (1976, 1977) have reported that certain widely used herbicidal formulations contained trace contaminations of *N*,*N*-dialkylnitrosamines. These nitrosamines have been shown to be carcinogenic in several animal species (Magee and Barnes, 1967) and are, thus, suspect human carcinogens (Lijinsky and Epstein, 1970). Three of the formulations were dimethylamine salts of acidic herbicides and were found to contain 0.3–640 ppm of *N*-nitrosodimethylamine (DMNA). One formulation of the dinitroaniline herbicide trifluralin (Treflan, a registered trademark of Elanco Products Co., Division of Eli Lilly and Co., for the herbicide trifluralin, α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) was found to contain 154 ppm of *N*-nitrosodi-*n*-propylamine (NDPA).

Trifluralin is one of a class of substituted dinitroanilines (DNA's) whose herbicidal properties were first reported by Alder et al. (1960). Several related chemicals are marketed by Elanco, including benefin (Balan, Balfin, *N*-butyl-*N*-ethyl-2,6-dinitro-4-(trifluoromethyl)benenamine), isopropalin (Paarlan, 2,6-dinitro-*N*,*N*-dipropylcumidine), and ethalfluralin (Sonalan, *N*-ethyl-*N*-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)-benzenamine). The herbicides oryzalin (Surflan, 3,5-dinitro-N^4,N^4-dipropylsulfanilamide) and prosulfalin (Sward, *N*-[[4-(dipropylamino-3,5-dinitrophenyl]sulfonyl]-*S*,*S*-dimethylsulfilimine), also possess structural similarities to trifluralin. In addition, several products are marketed by other manufacturers which contain the dinitroaniline moiety. The United States Environmental Protection Agency has determined that products containing any of these chemicals may pose a *N*-nitroso problem and have required that all such products be analyzed for the presence of *N*-nitroso contaminants (Environmental Protection Agency, 1977).

The NDPA content in Treflan was detected by Ross et al. (1976) using a pyrolytic, chemiluminescent detector called the thermal energy analyzer (TEA). This detector was first described by Fine et al. (1973) and its theoretical basis was discussed in a later article (Fine et al., 1975). For the determination of NDPA in Treflan, the TEA was coupled to a gas chromatograph (GC–TEA), a system originally described by Fine and Rounbehler (1975). Briefly, nitrosamines which elute from the GC are catalytically pyrolyzed to produce the nitrosyl radical (NO·). Other pyrolysates are cryogenically trapped and the nitrosyl radical is reacted with ozone to produce electronically excited nitrogen dioxide (NO_2*). This species relaxes with the emission of light which is detected by means of a photomultiplier tube. The system is very specific for the detection and determination of volatile nitrosamines.

In the initial report (Ross et al., 1976), NDPA was determined by injecting a solution of Treflan 4EC directly into a GC–TEA system without prior cleanup. This procedure is satisfactory for a single sample, but additional cleanup steps are necessary for the efficient processing of a large number of samples and to prolong the utility of GC columns. Furthermore, a subsequent reduction in the level of nitrosamine contaminants in dinitroaniline products necessitated a concentration of the contaminants to obtain valid analytical data. In this report, analytical methods are described for the highly sensitive and selective determination of volatile nitrosamines in technical and formulated products of several dinitroaniline herbicides.

MATERIALS AND METHODS

Chemicals and Apparatus. Reference standard nitrosamines (NAs) were obtained from commercial sources or were prepared from the corresponding secondary amines by the method of Preussman (1962). These included *N*-nitrosodimethylamine (DMNA), *N*-nitrosodiethylamine (DENA), *N*-nitroso-*N*-ethyl-*N*-(2-methylallyl)amine (EMANA), *N*-nitroso-di-*n*-propylamine (NDPA), and *N*-nitroso-*N*-*n*-butyl-*N*-ethylamine (BENA). The solvents employed were distilled in glass prior to use. Anhydrous sodium sulfate was washed with methanol and air-dried to remove interfering substances. Alumina, Alcoa F-20, was deactivated by adding sufficient deionized water to yield a moisture content of 4% and tumbling for 1 h in a closed container. Standard solutions were prepared in actinic or foil-wrapped glassware and laboratory operations were conducted under yellow fluorescent lighting to prevent photodegradation of nitrosamines.

Chromatographic columns consisted of 250 mm × 14 mm i.d. glass tubes equipped with removable Teflon stopcocks and glass tips and attached 250-mL reservoirs. Concentration steps were accomplished using rotary vacuum evaporators (Rinco) and 35–40 °C water bath. All measurements were made on a gas chromatograph–thermal energy analyzer (GC–TEA) system consisting of a Thermo Electron Model 661 single-column gas chromatograph interfaced to a Thermo Electron TEA Model 502 detector. The GC column was a 500 cm × 2 mm i.d. stainless steel tube packed with 10% SP-1000 on 100/120 mesh Chromosorb WAW (Supelco, Inc., Bellefonte, PA). The column oven was maintained at 185 °C and the flow rate of argon through the column was adjusted to 15 mL/min. The pyrolysis oven of the TEA was operated at 450 °C and the cold trap medium consisted of ethanol maintained as a slush by periodic addition of liquid nitrogen. The recorder (Hewlett-Packard Model 7123A) was operated at a chart speed of 0.5 cm/min.

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Procedures. *Technical Materials.* The DNAs of low polarity, namely, trifluralin, benefin, ethalfluralin, and isopropalin, exhibit low melting points, and representative samples were most readily obtained by completely melting the entire sample in a 70 °C sand or water bath. (Technical isopropalin is normally a liquid at room temperature.) After mixing the melted sample, a 0.1–0.5 g portion was weighed into a small vial and dissolved in 2 mL of 1-chlorobutane. Oryzalin and prosulfalin, which are high melting crystalline materials, were weighed without prior melting and dissolved in 2 mL of ethyl acetate.

Emulsifiable Concentrates. The lower polarity DNAs formulated as emulsifiable (EC) or liquid (LC) concentrates were weighed (0.2–0.5 g) into vials and dissolved in 2 mL of 1-chlorobutane.

Wettable Powders. Wettable powder formulations of oryzalin and prosulfalin were weighed (1 g) into conical flasks and slurried with 100 mL of ethyl acetate for 10 min using a magnetic stirrer. The insoluble material was allowed to settle and a 10–15-mL aliquot of the supernatant solution was concentrated to about 2 mL prior to column chromatography.

Granules. Granules (2.5 g) which did not contain vermiculite were slurried with 100 mL of CH_2Cl_2 for 30 min using magnetic stirrers. The solids were allowed to settle and the supernatant solution was decanted through a plug of glass wool in a funnel. The extraction flask and residual solids were rinsed with 25 mL of CH_2Cl_2, 30 mL of 1-chlorobutane was added to the extract, and the resulting solution was concentrated to about 2 mL on a rotary vacuum evaporator.

Granules containing vermiculite (2.5 g) were extracted by the Soxhlet method for 8–16 h with 200 mL of CH_2Cl_2. The extract was mixed with 30 mL of 1-chlorobutane and the total volume was reduced to about 2 mL on a rotary vacuum evaporator.

Recovery Standard and Blank. Blanks and recovery standards were processed with each set of samples. If available, blank carriers or highly purified technical samples were fortified with the appropriate nitrosamine, usually at the 1-ppm level. In the absence of suitable blank materials, system blanks and system recoveries were processed through each step of the procedure employed.

Column Chromatography. *Preparation and Standardization.* Prior to use, each batch of alumina was standardized to determine the elution pattern of the volatile nitrosamines. A column was prepared by placing a glass wool plug in the bottom of a glass column and adding 11.5 g (13 mL) of 4% deactivated alumina, followed by 1–2 cm of anhydrous sodium sulfate. The column was washed with 30 mL of 1-chlorobutane. (Alternatively, the column may be wet-packed in hexane or 1-chlorobutane.) To check the elution characteristics of the column, a 1-chlorobutane solution containing 2.5 μg of both DMNA and NDPA was placed on the column and the liquid was drained to the top of the column. The column was eluted with 50 mL of hexane, followed by six 20-mL portions of 1-chlorobutane. Each eluate fraction was collected and analyzed for nitrosamine content. With properly prepared alumina, the nitrosamines eluted in the 20–80-mL fraction of 1-chlorobutane. (Note: Benzene was used in early work instead of 1-chlorobutane and was a suitable eluting solvent.)

Low Polarity DNAs. Sample solutions of the lower polarity DNAs in 1-chlorobutane were placed directly on separate alumina columns. The liquid was drained to the top of the columns, and sample vials were rinsed with two 3-mL portions of hexane which were added to the columns. The column was washed with 45 mL of hexane, followed by 20 mL of 1-chlorobutane, which removed most of the DNA from the columns. The eluates to this point were discarded. The NAs were eluted from the columns with 100 mL of 1-chlorobutane. The eluate was concentrated to about 0.5 mL, quantitatively transferred to 2-mL volumetric flasks, and diluted to volume with 1-chlorobutane.

High Polarity DNAs. The higher polarity DNAs, oryzalin and prosulfalin, required the use of two sequential alumina columns. Two identical columns were prepared for each sample, blank, and recovery. Sample solutions in 2–3 mL of ethyl acetate, a solvent blank (2 mL of ethyl acetate), and 2 mL of a standard solution of NDPA in ethyl acetate were placed on separate columns. The liquid was drained to the top of each column and the sample vials were rinsed with two 3-mL portions of 1-chlorobutane which were added to the columns. The liquid was drained to the top of the columns while commencing the collection of eluate in 125-mL boiling flasks. The columns were then eluted with 75 mL of 1-chlorobutane, which removed the NA and a small amount of the herbicide. The eluates were concentrated to about 2–3 mL and the residual solutions were quantitatively transferred to the second set of alumina columns. The columns were washed with 50 mL of hexane and 20 mL of 1-chlorobutane, and these washings were discarded. The NDPA was eluted from the columns with 100 mL of 1-chlorobutane. The eluate was concentrated to about 0.5 mL, quantitatively transferred to 2-mL volumetric flasks, and diluted to volume with 1-chlorobutane.

Measurement. The response characteristics of the GC–TEA were ascertained by injecting 5 μL of 0.5 μg/mL solutions of the appropriate NAs. The instrument attenuator was normally set at 8 for these standard injections. For blanks, recoveries, and samples, 5 μL of the purified solutions were injected at attenuation 4, and the attenuator was manually adjusted to keep the peak "on chart". If weak or no responses were observed for the sample solutions, a 50-μL aliquot was injected at attenuation 4. In these cases, 50 μL of 0.05 μg/mL solutions of NAs were injected for reference purposes.

The amount of volatile nitrosamine in a formulation or technical product was calculated from the peak height responses in the samples compared to the direct standards. All results were corrected for recovery efficiency.

RESULTS AND DISCUSSION

Volatile nitrosamines were handled with extreme caution. Any contact of the substance with skin and clothing was avoided. Neat and concentrated solutions were handled and stored in a glovebox to avoid contact. The exhaust air from the glovebox was passed through a charcoal filter and vented outside the laboratory to minimize sample contamination and personnel exposure.

Nitrosamines are sensitive to photolytic degradation and exposure of samples and solutions to light during processing was minimized to assure valid analytical data. Equipping laboratory work areas with yellow fluorescent lighting was a suitable preventive measure.

Laboratory solvents, especially dichloromethane, were redistilled in glass to remove interfering substances. Even redistilled dichloromethane has yielded GC–TEA responses at the retention time of DENA if care were not taken to select the proper distillation fraction. Some lots of anhydrous sodium sulfate have been found to contain TEA-responsive impurities and all lots were washed with methanol prior to use. All glassware, especially separatory

funnels and boiling flasks, were rinsed with acetone to minimize contamination from previous sample runs. Each rotary evaporator was rinsed thoroughly with acetone prior to evaporating each sample.

Because the TEA is a highly sensitive detector, carryover or memory effects have been observed with some GC columns. To eliminate false positives from this source, a 50-μL aliquot of solvent was injected after any sample which required an attenuation setting of 32 or greater to keep the NA response on scale.

The alumina must be properly deactivated in order to separate the volatile nitrosamines from the dinitroaniline herbicides. For optimum results, the NAs should elute in the 20–80 mL 1-chlorobutane fraction. Insufficient deactivation will result in larger volumes of solvent being required for the complete elution of the NAs. Each batch of alumina should be checked by the standardization procedure described.

The low polarity DNA herbicides eluted from the alumina column ahead of the nitrosamine contaminants using the elution scheme described. Some faint color was observed in most NA fractions, which was probably due to some other higher polarity impurities in the original samples. The column described readily separated 0.5 g of herbicide from any volatile nitrosamine present. Up to 5 g of technical product has been successfully chromatographed when done carefully, but this is not recommended on a routine basis.

The higher polarity DNAs, such as oryzalin, were not eluted from alumina with 1-chlorobutane or benzene, which permitted their separation from the NA contaminants. However, oryzalin and prosulfalin were insufficiently soluble in solvents of polarity equivalent to or less than 1-chlorobutane and had to be placed on the columns in a more polar solvent, ethyl acetate. The small amount (2–3 mL) of ethyl acetate added to the column brought some of the DNA and other impurities down the column with its front, resulting in a highly colored eluate fraction. Concentration and injection of this fraction into the GC–TEA resulted in a large "solvent peak", which limited the detectability of NDPA to about 1 ppm. The second column, prepared and eluted in the same manner as for the lower polarity DNAs, retained the herbicide and other colored impurities present in the first column eluate, and yielded a "clean" NA fraction for GC–TEA measurement.

Rotary vacuum evaporators (RVEs) were acceptable for the concentration of solutions of the volatile NAs under certain conditions. The water bath was kept at or below 40 °C and solutions were not allowed to evaporate to dryness. To minimize the latter occurrence, a "keeper solvent" (1-chlorobutane or benzene) was added when concentrating very volatile solvents, such as dichloromethane. The keeper solvent prevented the sudden evaporation of the last few drops of solution and consequent loss of the NA. Recoveries of all volatile NAs have exceeded 95% using this procedure. Lower recoveries of DMNA and DENA were observed during the evaporation of solutions of 1-chlorobutane alone, probably due to the longer time required for evaporation. Kuderna-Danish (KD) concentrators yielded better recoveries for DMNA and DENA, but were comparable to the RVEs for NDPA and BENA. However, the use of the KDs tends to be much more time consuming than the RVEs and the latter have proven to be more efficient for the processing of large numbers of samples.

The necessity for separating the herbicide and the NA contaminant is illustrated in Figure 1. To obtain this chromatogram, 102 mg of a sample of technical trifluralin

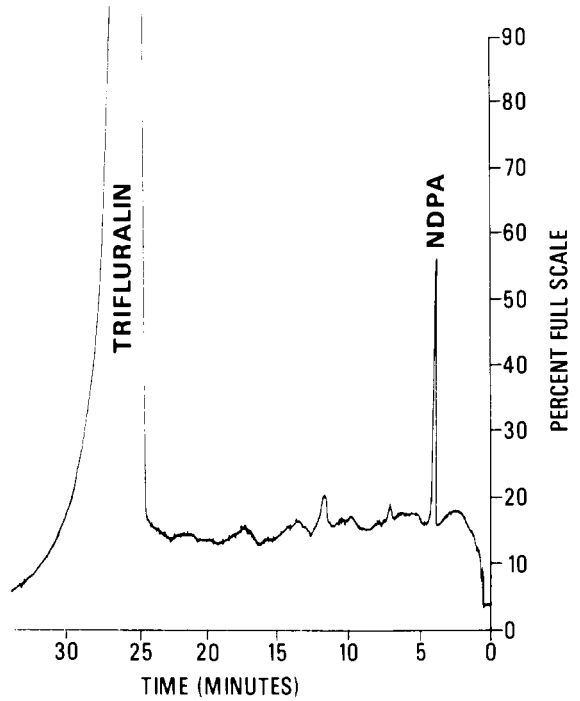

Figure 1. GC–TEA chromatogram of trifluralin technical, 10.2 mg/mL in CH_2Cl_2, 5 μL injected directly, ×8. NDPA response equivalent to 2.2 ng.

was dissolved in 10 mL of dichloromethane and 5 μL of the resulting solution was injected into the GC–TEA system. Since the trifluralin response was of no interest, several samples could be analyzed for NDPA content by overlapping sample injections. After about four such injections, the instrument was shut down for about 2 h to allow the trifluralin to clear the column. This procedure had the advantage of being direct, requiring no processing steps or recovery samples and was suitable for the measurement of just a few samples (6–10) per day, providing that a limit of detection of about 1 ppm was acceptable. Column life was short under these conditions and the red filter in the photomultiplier housing frequently became fogged, necessitating a 4–6-h shutdown of the TEA for cleaning.

The use of the alumina column permitted the analysis of many more samples per instrument per day with about the same accuracy as the direct method, providing correction was made for recovery efficiency. GC columns have lasted for several months and cleaning of the filter has been required only about monthly instead of weekly. In addition, isolation of the NAs with the alumina column procedure reduced the possibility of encountering false positives from TEA responsive compounds other than nitrosamines.

Some recovery data are summarized in Table I for NDPA, BENA, and EMANA. The NAs were added to specially purified trifluralin, technical oryzalin, or were obtained by fortifying the solvent system. Overall, recoveries of NDPA from trifluralin averaged 77.8% while the solvent system recoveries averaged 88.0%. This difference is not of great consequence when performing assays at the ppm level and the solvent system recovery is nearly as supportive of the method as the fortified sample recovery. Recoveries of BENA and EMANA have been similar to those observed for NDPA. The recoveries marked with the footnote *a* were obtained by the two-column oryzalin procedure. A wider range of recoveries was observed in this case but the averages were close to those observed by the one-column procedure.

Table I. Recoveries of Nitrosamines from Purified Trifluralin (TR), Oryzalin (OR), or Solvent Systems (SS)

nitrosamine	amt added, μg	substrate wt, mg	no. of runs	% recovery range	% recovery av
NDPA	0.98	TR, 100	13	65.8-100	79.8
NDPA	0.98	SS	20	63.9-102.9	87.3
NDPA	0.67	TR, 100	16	62.2-88.5	74.9
NDPA	0.67	SS	5	66.9-89.0	79.9
NDPA	0.54	SS	10	74.4-100	93.4
NDPA	0.49	TR, 100	3	82.6-95.1	88.6
NDPA	0.098	TR, 500	5	56.0-90.4	73.3
NDPA	0.049	TR, 500	3	78.9-79.4	79.1
NDPA	0.049	OR, 500[a]	7	50.6-100	80.5
NDPA	0.67	OR, 500[a]	2	71.7-73.2	72.5
NDPA	0.50	SS	5	58.5-93.8	74.2
BENA	0.93	SS	2	88.0-92.0	90.0
BENA	0.54	SS	5	74.1-96.9	88.1
BENA	0.68	TR, 200	1	86.0	
EMANA	1.08	TR, 100	5	52.1-93.4	78.8
EMANA	0.72	SS	4	72.4-91.0	84.6

[a] Processed through the two-column oryzalin procedure.

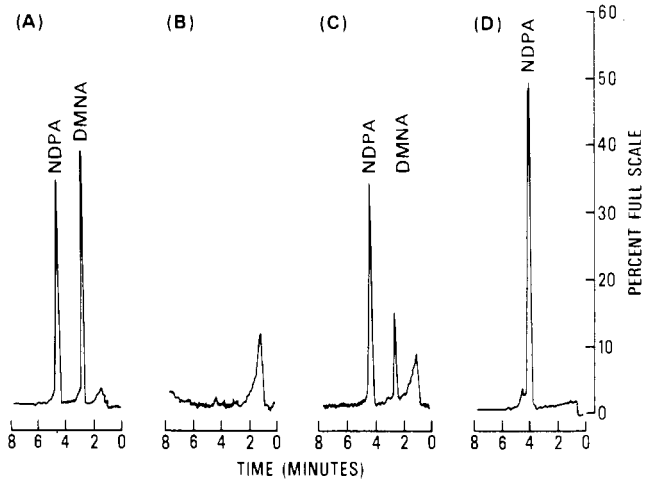

Figure 2. GC–TEA chromatograms for determination of NDPA in trifluralin technical. (A) Direct standards; DMNA, 0.24 μg/mL, and NDPA, 0.38 μg/mL, ×8. (B) Reagent blank, ×4. (C) System recovery, 0.24 and 0.38 μg, DMNA and NDPA, 34 and 98%, respectively, ×4. (D) Lot 1MU12 trifluralin, 282 mg, ×16, 8.2 ppm NDPA. Injection volume, 5 μL.

Recovery data from granular carriers are summarized in Table II. Several herbicidal products containing benefin and trifluralin have been examined for nitrosamine content. Recoveries were run with each set of samples by fortifying blank carrier with the NA and processing these with the samples. Recovery efficiencies for BENA and NDPA were comparable. Those granules containing clays, cobs, limestone, and activated sludge were generally assayed by the slurry method, while vermiculite carriers required Soxhlet extraction. The slurry method was preferred for fertilizer-based carriers since Soxhlet extracts of such products occasionally exhibited large "solvent peaks", whereas such responses were small with the slurry technique. However, fertilizer products on vermiculite required Soxhlet extraction to obtain recoveries above 60%. Use of the slurry method with products containing vermiculite resulted in recovery efficiencies in the 20–40% range.

The low recoveries of DMNA in Table II were observed with either extraction technique. Some of the losses of DMNA occurred during the concentration with the rotary vacuum evaporators.

Chromatograms from three typical assays are presented in Figures 2, 3, and 4. A determination of NDPA in a sample of trifluralin technical is shown in Figure 2. The system recovery of NDPA in this case was 98% and the sample contained 8.2 ppm of NDPA. The small response following the NDPA in the sample chromatogram is due

Table II. Recoveries of Nitrosamines from Granular Carriers

nitrosamine	amt. added to 2.5 g, μg	carrier	no. of runs	% recovery range	% recovery average
NDPA	0.5	fertilizer	3	61.8-95.2	76.5
NDPA	0.5	misc.[a]	3	72.3-83.7	78.4
BENA	1.08	fertilizer	3	64.5-72.3	69.1
BENA	0.54	fertilizer	10	51.1-90.0	74.9
BENA	0.54	vermiculite	6	55.4-90.7	70.4
BENA	0.54	misc.	6	61.7-98.0	81.0
DMNA	0.24	fertilizer	5	15.3-33.4	25.3
DMNA	0.24	vermiculite	2	23.5-26.8	25.2

[a] Misc. includes clays, corn cobs, limestone, and activated sludge.

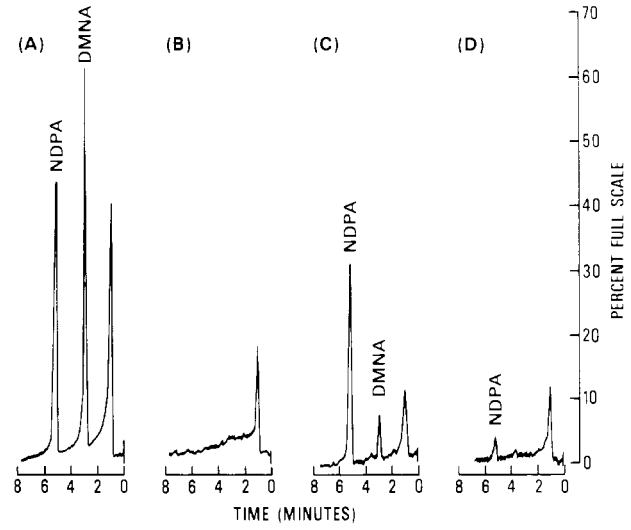

Figure 3. GC–TEA chromatograms for determination of NDPA in SURFLAN 75W. (A) Direct standards; DMNA, 0.34 μg/mL, and NDPA, 0.50 μg/mL, ×8. (B) Reagent blank, ×4. (C) System recovery, 0.34 and 0.50 μg of DMNA and NDPA, 11 and 74%, respectively, ×4. (D) SURFLAN 75W, 343 mg, ×4, 0.2 ppm NDPA. Injection volume, 5 μL.

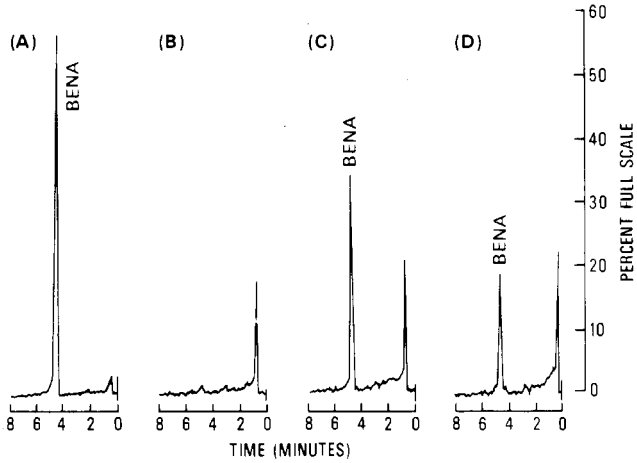

Figure 4. GC–TEA chromatograms from determination of BENA in a lawn fertilizer (12-2-4) vermiculite granule with benefin (0.43%). (A) BENA, 0.54 μg/mL, ×8. (B) Carrier blank, 2.5 g, ×4. (C) Recovery, 0.54 μg BENA + 2.5 g carrier blank, ×4, 60%. (D) Sample, 2.5 g, ×4, 0.1 ppm BENA. Injection volume, 5 μL.

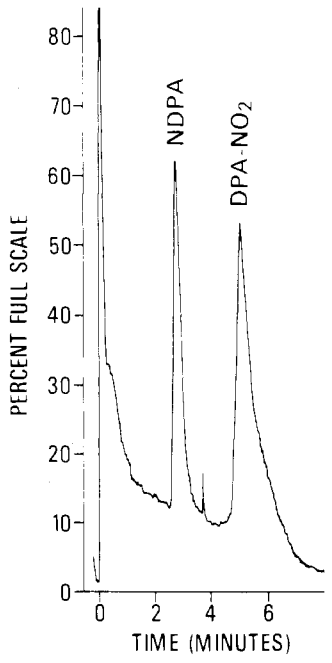

Figure 5. GC–TEA chromatogram of trifluralin technical, 1.0 g, alumina column cleanup concentrated to 2.0 mL of benzene, 50 μL injected at ×4. NDPA and DPA-NO_2 response equivalent to 0.4 and 0.3 ppm, respectively.

to a seven-carbon nitrosamine as determined by GC–mass spectrometry, but its exact structure is unknown. It probably arises from an impurity in the dipropylamine used in the trifluralin synthesis.

Figure 3 contains chromatograms from an NDPA determination in SURFLAN 75W. The NDPA recovery was 74% through the two-column procedure and the sample contained 0.2 ppm of NDPA.

The chromatograms in Figure 4 are from a determination of BENA in a lawn fertilizer on a vermiculite carrier which contained 0.43% benefin. The Soxhlet method was used on these samples. The recovery was 60% and the sample was found to contain 0.1 ppm of BENA.

The direct standards and recoveries in Figures 2 and 3 contained DMNA in addition to NDPA. The recovery of DMNA through the one-column procedure was 34% while through the two-column procedure it was only 11%. DMNA was included in these and other assays to serve as a reference should responses other than NDPA be observed in blanks or samples.

The peak height response obtained with the GC–TEA is a linear function of attenuation for the entire range of the attenuator (Fine and Rounbehler, 1975). Consequently, it was valid to keep peaks "on scale" by attenuation rather than dilution of the sample.

The sensitivity of the method for NDPA, BENA, or EMANA was about 0.1 ppm when a 0.5-g sample was analyzed and 5 μL of the final purified solution was injected. This was equivalent to the injection of about 0.1 ng of nitrosamine, which is in agreement with the limits of detection reported by Fine and Rounbehler (1975). The sensitivity could be increased to 0.01 ppm by injecting 50 μL of final solution or by increasing the sample size. Up to 10 g of some granules can be extracted and processed for analysis.

The alumina column cleanup procedure has been successfully applied to other dinitroaniline herbicides and to extracts of highly colored manufacturing waste treatment samples. The sensitivity was dependent upon the sample size selected and the 0.1-ng limit of detection of the nitrosamine.

The volatile nitrosamines of interest have generally been the only TEA-responsive substances observed in DNA herbicidal products following the alumina column, with one exception. A few samples of technical trifluralin exhibited a TEA peak at a retention of 1.8 relative to NDPA (Figure 5). This response, initially suspected of being another nitrosamine, was identified as *N*-nitrodi-*n*-propylamine (DPA-NO_2) by GC–MS and the preparation of authentic material. Hotchkiss et al. (1978) have made a similar observation and identification on a sample of Treflan EC and noted the potential for misidentifying TEA responses in dinitroaniline chemicals.

In the application of these procedures to unknown samples, consideration must be given to possible artifact formation during sample processing. Reagents and/or samples may contain traces of nitrosating agents or nitrosatable compounds which may react and yield false positives. Krull et al. (1978) have adequately dealt with the subject and suggest the addition of nitrosation inhibitors to all samples prior to analysis. Ammonium sulfamate has been found to be a suitable inhibitor in our laboratories and is added to samples periodically to confirm that artifacts are not being observed.

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