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# CONFIRMING THE PRESENCE OF N-NITROSAMINES IN AMBIENT AIR AND CIGARETTE SMOKE BY CONVERTING TO AND PHOTOCHEMICALLY ALTERING THEIR CORRESPONDING N-NITROAMINES

JOHN A. CUCCO*
*Rhode Island Department of Health, Air Pollution Laboratory, Providence, RI 02904 (U.S.A.)*
and
PHYLLIS R. BROWN
*University of Rhode Island, Department of Chemistry, Kingston, RI 02881 (U.S.A.)*
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## SUMMARY

An analytical procedure for the detection of N-nitrosamines, which is one of the most sensitive available, has been expanded to make the technique more selective. This procedure involves oxidizing the nitrosamines to their corresponding nitroamines, with subsequent detection of picogram quantities by gas chromatography with an electron-capture detector. The presence of the nitroamines is then confirmed by photochemically altering them using a UV lamp and observing if the resulting decrease in peak height with time of irradiation obeys rate expressions derived by using reference nitroamines. The results of analyses of ambient air and cigarette smoke samples for the presence of nitrosamines are presented.

## INTRODUCTION

To detect nitrosamines in ambient air or cigarette smoke, a technique is desirable that is capable of detecting picogram quantities. Of the analytical techniques[1–8] that have been used to detect nitrosamines in a variety of media, few are capable of achieving this sensitivity. In addition to sensitivity, selectivity is an important consideration, especially since questionable results obtained in the past may be attributed to the presence of interfering substances[7,9]. At present, a gas chromatograph with a mass spectrometer[7] and a gas chromatograph with a thermal energy analyzer detector[10] are considered to be the most selective techniques. However, these detectors are not commonly found in analytical laboratories. Therefore, an alternative procedure was developed whereby the more readily available electron-capture detector (ECD) can be used.

One of the most sensitive methods used for the analysis of nitrosamines in foods involves oxidizing the nitrosamines to their corresponding nitroamines; a gas chromatograph with an ECD is then used to detect the resulting nitroamines at the picogram level[11–14]. It is this technique that has been expanded and coupled with a

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newly developed, highly selective, confirmatory test. This confirmatory test is based on the fact that nitroamines, which are strong electron capturers, are converted into relatively weak electron-capturing compounds when irradiated with short-wave UV light[15,16]. By irradiating nitroamine standards under set conditions for different periods, a photochemical rate constant was derived for each nitroamine. These rate constants were then used to characterize the specific nitroamines, since the observed decreases in peak heights were correlated with time of irradiation. Further verification was obtained by two-column confirmation.

## EXPERIMENTAL

### *Apparatus*

Gas chromatograph (Tracor MT 220); Kuderna–Danish evaporators (25-ml capacity concentrator tubes with three-stage Snyder columns) and Chromaflex chromatography columns, 30 cm × 1 cm I.D. (Kontes Glass); short-wave (germicidal) UV lamp (Spectroline TF-250); vacuum pump (Metal Bellows MB-41); midget impingers with 75-ml capacity bottles (Ace Glass).

### *Reagents*

Pesticide-grade pentane, heptane and ethyl acetate (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) and methylene chloride (Mallinckrodt, St. Louis, MO, U.S.A.); neutral alumina, activity I (ICN Pharmaceuticals, Cleveland, OH, U.S.A.): trifluoroacetic acid (Mallinckrodt, organic reagent); 50% hydrogen peroxide (Fisher Scientific, Pittsburgh, PA, U.S.A.; certified); anhydrous diethyl ether (Fisher ACS).

### *Standards*

Dimethyl- and diethylnitroamines were synthesized by nitrolyzing the corresponding N,N-dialkylformamides with nitric acid in a solvent of trifluoroacetic anhydride[17]. A stock standard solution was prepared by dissolving approximately 10 mg of each nitroamine in 100 ml of ethyl acetate; subsequent dilutions were made in heptane. Standard curves were constructed after injecting standards on to both Reoplex and Carbowax columns. Standards were stored at room temperature, shielded from direct exposure to light.

### *Irradiation experiment*

Standard solutions containing both dimethyl- and diethylnitroamines were irradiated in quartz cuvettes for various periods; the samples were situated 4 cm from a 25-W short-wave UV lamp. After each irradiation, 5 $\mu$l was injected on to both Carbowax and Reoplex columns. Plots of the log of the number of picograms per 5-$\mu$l injection *vs.* time of irradiation in seconds, were constructed. The resulting slopes were recorded.

### *Ambient air sampling sites*

Ambient air samples were taken at two sites in Rhode Island; four samples at a site in Providence and four at a rural site in West Greenwich. These samples were taken on different days under different meteorological conditions.

*Ambient air sample collection*

Ambient air was bubbled through a trap containing 50 ml of 1 *N* potassium hydroxide for 90 min at a flow-rate of *ca.* 2 l/min; the trap was shielded from direct sunlight. After collection, the trap was rinsed with 10 ml of KOH, which was added to the 50-ml sample. The sample, stored in an all-glass flask, was returned to the laboratory for analysis.

*Sample work-up*

(1) The exposed KOH solution was extracted in a separatory funnel three times with 8-ml portions of methylene chloride ($CH_2Cl_2$). (2) After drying with anhydrous sodium sulfate, the extract was poured into a concentrator tube. The remaining sodium sulfate was rinsed several times with small portions of $CH_2Cl_2$, which were added to the concentrator tube until a total of 24 ml of $CH_2Cl_2$ extract had been collected. (3) A 6-ml portion of the $CH_2Cl_2$ extract was pipetted into a stoppered vial and stored in a refrigerator. (4) The remaining 18 ml of extract was evaporated in a Kuderna–Danish (KD) evaporator to a volume of 1 ml; the temperature of the water bath was maintained between 52 and 55°C. (5) Then 1 ml of distilled water was added to the KD through the Snyder column, and the resulting 2 ml of sample was transferred to a 50-ml stoppered flask using a pasteur pipette. (6) Trifluoroacetic acid (5 ml) and 50% hydrogen peroxide solution (4 ml) were added, and the mixture was swirled for 30 sec, then allowed to react for 24 h. (7) The mixture was poured on to 15 g of crushed ice and neutralized using *ca.* 40 ml of 20% potassium carbonate solution. (8) The nitroamines were extracted in a separatory funnel three times with 8-ml portions of $CH_2Cl_2$. (9) The extract was dried over sodium sulphate and evaporated to 1 ml in a KD. (10) Pentane (4 ml) was added through the Snyder column, and the mixture saved for column clean-up.

*Column clean-up*

The following substances were added, in sequence, to a 30 × 1 cm I.D. chromatography column that was half filled with *n*-pentane; each substance was slowly added, with occasional tapping of the column to assist in settling[14].

(1) Neutral alumina (4 g; Brockmann activity III, prepared by adding 6 ml of water to 94 g of alumina activity I).

(2) Magnesium oxide (2 g).

(3) Enough sodium sulfate to fill *ca.* 1 cm of the column. Both the magnesium oxide and the sodium sulfate were purified by baking at 550°C for 6 h. The pentane was drained into the top of the sodium sulfate layer, and the column was washed by eluting with 25 ml of 50% (v/v) diethyl ether in pentane followed by 25 ml of pentane. (The column may not require washing if the components are of sufficient purity.) The sample (step 10 of the sample work-up) was added to the column and drained just into the sodium sulfate layer. The concentrator tube was washed with 2 ml of pentane, which was added to the column and again drained into the sodium sulfate layer. The column was then eluted with 25 ml of a 1% (v/v) solution of diethyl ether in pentane; this eluate was discarded. Next, the column was eluted with 35 ml of 25% (v/v) diethyl ether in pentane, and this 35 ml of eluate was concentrated in a KD evaporator to a final volume of *ca.* 0.5 ml. A water-bath temperature of between 46 and 50°C was used. Heptane was added through the Snyder column of the KD

until the concentrator tube contained 1 ml of sample. The concentrator tube was stoppered and the sample was saved for gas chromatographic analysis.

*Gas chromatographic analysis*

The concentrated extract was analyzed for nitroamines by using a gas chromatograph equipped with a tritium ECD. The columns and conditions used were: (1) A glass column (6 ft. × 0.250 in. O.D.) packed with 10% of Carbowax 20M on Chromosorb W/HP (80–100 mesh) operated isothermally at 160°C, with a nitrogen flow-rate of 70 ml/min; and (2) a similar column packed with 6% of Reoplex 400 on AW DMCS-treated Chromosorb W (60–80 mesh) and operated isothermally at 140°C, with a nitrogen flow-rate of 70 ml/min.

If the presence of a nitroamine was verified on both columns, then the 6-ml aliquot (from step 3 of the sample work-up) was analyzed for the presence of nitroamines or interfering species that may have been present in the ambient air sample. The 6-ml aliquot was concentrated to 1 ml in a KD evaporator, then 5 ml of pentane were added through the Snyder column, and the sample was again concentrated to 1 ml. This process of adding pentane and concentrating was repeated twice more, and a final 0.5 ml of extract was analyzed on the gas chromatograph.

*Cigarette smoke samples*

Four cigarettes were smoked, two at a time, with the lit ends inserted into a 250-ml side-arm vacuum flask; each cigarette was puffed once every 30 sec. The side-arm of the flask was connected to the inlet of a midget impinger by a piece of PTFE tubing; the impinger bottle contained 50 ml of 1 *N* KOH. The sample was drawn from the flask at a rate of 2 l/min for a total sampling time of *ca.* 14 min. After collection, the trap was rinsed with 10 ml of KOH, which was added to the 50-ml sample. The sample work-up, column clean-up, gas chromatographic analysis and irradiation procedures were carried out exactly as for the ambient air samples. In addition, two modifications in the overall procedure were used to improve the isolation of the peak corresponding to dimethylnitroamine.

*Modification A.* A pre-oxidation clean-up of the cigarette smoke extract was performed using the same column as was used for the post-oxidation clean-up of the ambient air extracts[14]. After performing step 4 of the sample work-up, the 1 ml of $CH_2Cl_2$ extract was diluted with 4 ml of pentane and transferred to the top of the clean-up column. The sample was drained just into the sodium sulfate layer. The concentrator tube was washed with 2 ml of pentane, which was added to the column and again drained into the sodium sulfate layer. The column was then eluted with 50 ml of a 1% (v/v) solution of $CH_2Cl_2$ in pentane; this eluate was discarded. Next, the column was eluted with 50 ml of a 50% (v/v) solution of $CH_2Cl_2$ in pentane, this eluate being concentrated in a KD evaporator to a volume of 1 ml. The remaining steps of the procedure were carried out (continuing with step 5 of the sample work-up). In addition, following the oxidation of the sample, a modification to the post-oxidation clean-up was carried out (Modification B).

*Modification B.* Instead of collecting one 35-ml fraction [25% (v/v) diethyl ether in pentane] from the post-oxidation clean-up column, two separate fractions were collected. The first 20 ml were collected in one flask, while the remaining 15 ml were collected in another. Each fraction was then concentrated and analyzed. In

testing this procedure with nitroamine standards, it was observed that the first (20-ml) fraction quantitatively contained the diethylnitroamine, while the second (15-ml) fraction quantitatively contained the dimethylnitroamine.

*Sample analysis and trap efficiencies*

Analysis recovery experiments were conducted by adding different amounts of dimethyl- and diethylnitrosamine to 60-ml portions of 1 *N* KOH and carrying out the entire analysis procedure that was used for the ambient air samples. In addition, the following experiment was performed to determine whether the KOH trap was capable of quantitatively trapping both dimethyl- and diethylnitrosamine. To a 250-ml vacuum flask were added 130 ng of dimethylnitrosamine and 91 ng of diethylnitrosamine. The side-arm of the flask was connected to the inlet of the KOH trap, and 180 l of room air were pulled through the vacuum flask and into the trap at a flow-rate of 2 l/min for 90 min. The sample was then analyzed, as were the ambient air samples, and the efficiency of the KOH trap was determined.

*Testing for artifact formation*

To show that dimethylnitrosamine was not formed during the collection or work-up of the cigarette smoke samples, through the reaction of nitrite ions (or other nitrosating agents present in the sample) with dimethylamine, the following experiment was performed.

Two midget impingers were connected via a "T" to a common side-arm vacuum flask. To one of the impinger bottles was added 0.5 ml of an aqueous solution containing 272 $\mu$g of dimethylamine and 0.5 ml of an aqueous solution containing 272 $\mu$g of sodium nitrite. Four cigarettes were smoked (two at a time) with tips inserted in the flask for a total sampling time of 14 min. The inlet flow through each impinger was 1.2 l/min. The KOH solutions were then extracted and analyzed, along with a KOH blank to which 272 $\mu$g of dimethylamine was added.

## RESULTS AND DISCUSSION

Dimethyl- and diethylnitroamine were prepared in good yields. The purity of each was verified by determining its melting or boiling point and IR spectrum. The standard curve obtained using the Reoplex column is shown in Fig. 1. The retention times of dimethyl- and diethylnitroamine on this column are 2.30 and 2.93 min, respectively, while on the Carbowax column the corresponding retention times are 2.62 and 3.16 min.

A standard solution containing 0.0568 ppm of dimethylnitroamine and 0.0714 ppm of diethylnitroamine was irradiated with the UV lamp for different periods. After each irradiation, 5 $\mu$l of the resulting solution was injected on to the Reoplex column (Fig. 2). Fig. 3 is a graphic presentation of the decrease in concentration of nitroamines with time of irradiation. This photo-irradiation experiment was conducted six times over a 6-month period. The range of the slope for dimethylnitroamine (Fig. 3) was calculated to be $-4.4$ to $-4.8 \times 10^{-3}$ (average value $-4.7 \times 10^{-3}$), while the range for diethylnitroamine was $-5.8$ to $-6.2 \times 10^{-3}$ (average value $-6.0 \times 10^{-3}$). By using the average values for the slopes in the following

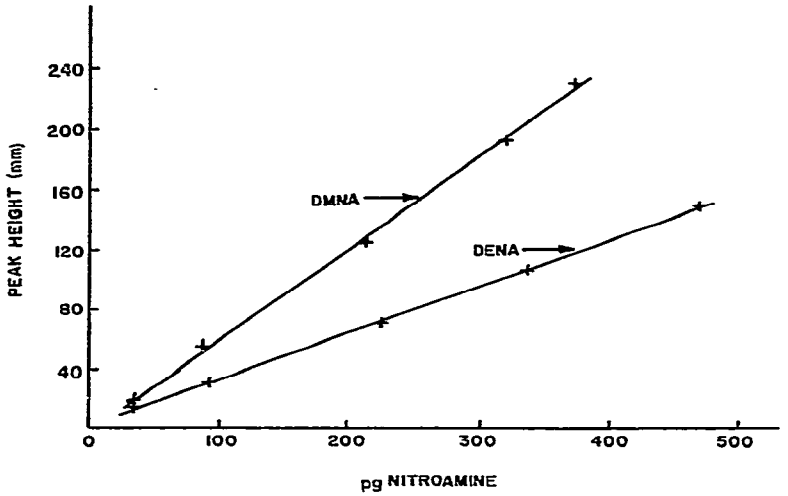


Fig. 1. Standard graphs for dimethylnitroamine (DMNA) and diethylnitroamine (DENA).

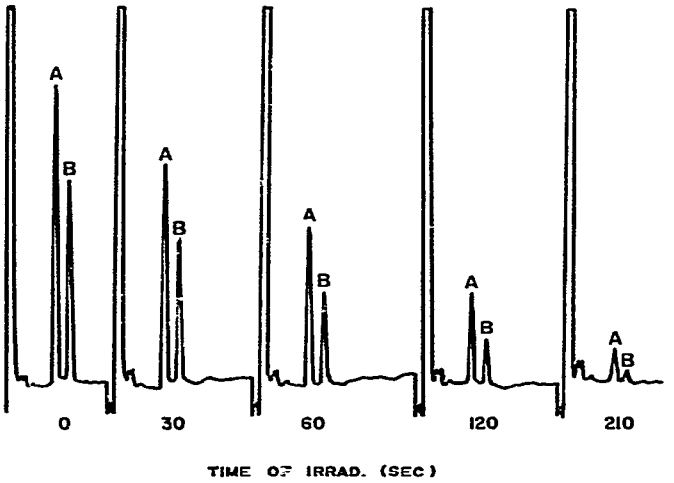


Fig. 2. Irradiation of a standard containing 0.0568 ppm of DMNA (peaks A) and 0.0714 ppm of DENA (peaks B).

equations, it is possible to predict, to within 6%, the decrease in peak height after irradiating a sample for a time ($t$) of 60 sec.

$$\log \text{dimethylnitroamine content (pg) after irradiation} = -4.7 \times 10^{-3}\, t + \log \text{dimethylnitroamine content (pg) before irradiation}$$

$$\log \text{diethylnitroamine content (pg) after irradiation} = -6.0 \times 10^{-3}\, t + \log \text{diethylnitroamine content (pg) before irradiation}$$

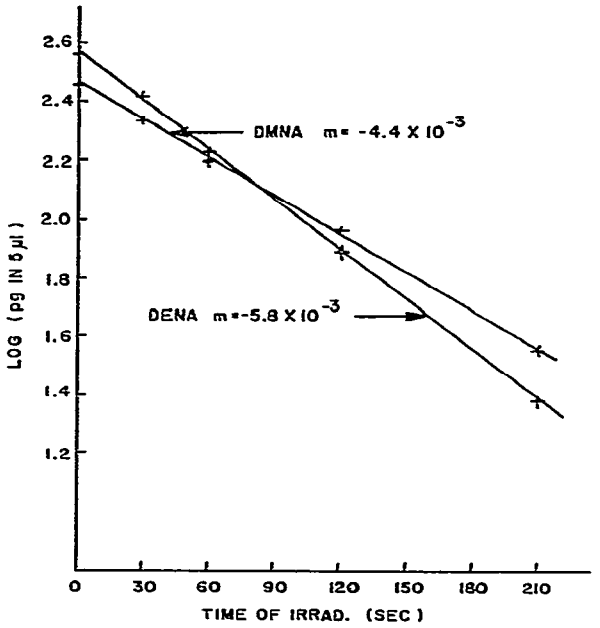


Fig. 3. Photoirradiation of a standard containing 0.0568 ppm of DMNA and 0.0714 ppm of DENA.

To date, only a limited number of air samples has been tested. Of the eight samples that were analyzed, only one was found to contain trace levels of both dimethyl- and diethylnitrosamine. The chromatograms in Fig. 4 show: (a) a blank carried through the total procedure, (b) the air sample with peaks corresponding to

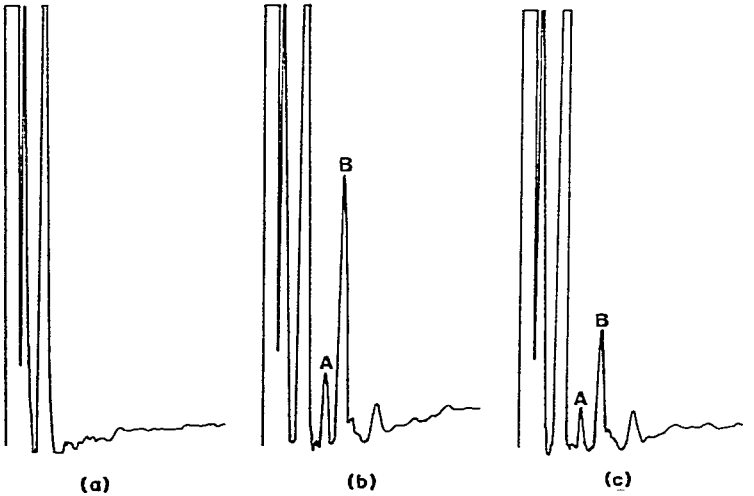


Fig. 4. Ambient air sample: (a) blank carried through the total procedure; (b) ambient air sample: peak A corresponds to an ambient air concentration of 0.044 ppb of dimethylnitrosamine (DMN); peak B to 0.256 ppb of diethylnitrosamine (DEN); (c) ambient air sample after irradiating for 60 sec with a short-wave UV lamp.

ambient air concentrations of 0.044 ppb of dimethylnitrosamine and 0.256 ppb of diethylnitrosamine (confirmed on Carbowax and Reoplex columns), and (c) the air sample after irradiating for 60 sec with short-wave UV light. The resulting peak heights in chromatogram (c) are both within 5% of their theoretically calculated values. Additional sampling is planned at the site where trace amounts were detected. If future samples are found to contain nitrosamines, then the tests for artifact formation, as described by Fine *et al.*[10] and by Krull *et al.*[19], will be performed to ensure that the nitrosamines were not formed during the sample collection or work-up.

The analysis of the extract from the smoke of four American brands of cigarettes showed the presence of dimethylnitrosamine. Fig. 5a is the chromatogram obtained after collecting the last 15 ml of eluate from the post-oxidation clean-up column, concentrating to 1 ml and injecting 5 $\mu$l on to the Reoplex column. The labeled peak represents 105.7 pg of dimethylnitroamine. In addition, a 5-$\mu$l injection on the Carbowax column gave a peak corresponding to 109.5 pg of dimethylnitroamine. If it is assumed that 10% of the cigarette smoke was trapped and the remaining 90% escaped through the top of the flask, then it can be estimated that each cigarette contained approximately 120 ng of dimethylnitrosamine (side-stream smoke). Upon irradiating this sample for 60 sec, photoreaction rate constants of $2.5 \times 10^{-3}$ sec$^{-1}$ and $2.7 \times 10^{-3}$ sec$^{-1}$ were calculated, based on peak-height drops observed on the Carbowax and Reoplex (Fig. 5b) columns, respectively. Since these rates are *ca.* 45% less than the expected average rate of $4.7 \times 10^{-3}$ sec$^{-1}$, the peak either does not represent dimethylnitroamine or there is an interfering substance(s) present. To prove or disprove the presence of the nitroamine, the following test was performed: A few $\mu$l of a concentrated dimethyl- and diethylnitroamine standard were added to the 1 ml of UV-irradiated cigarette smoke sample mentioned above. Fig. 6a represents a 7-$\mu$l injection of the resulting sample on to the Reoplex column. After irradiating this sample for a total of 60, 120 and 240 sec, the reaction rates were calculated to be $2.7 \times 10^{-3}$ sec$^{-1}$ $\pm$ $0.3 \times 10^{-3}$ sec$^{-1}$ for dimethylnitroamine and

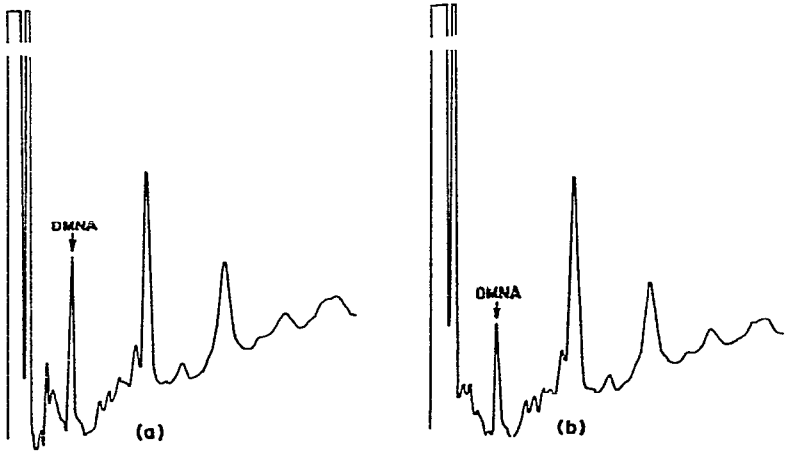


Fig. 5. Cigarette smoke sample: (a) side-stream smoke from four American brand cigarettes (labelled peak represents 105.7 pg of DMNA); (b) sample irradiated for 60 sec (labelled peak represents 72.8 pg of DMNA).

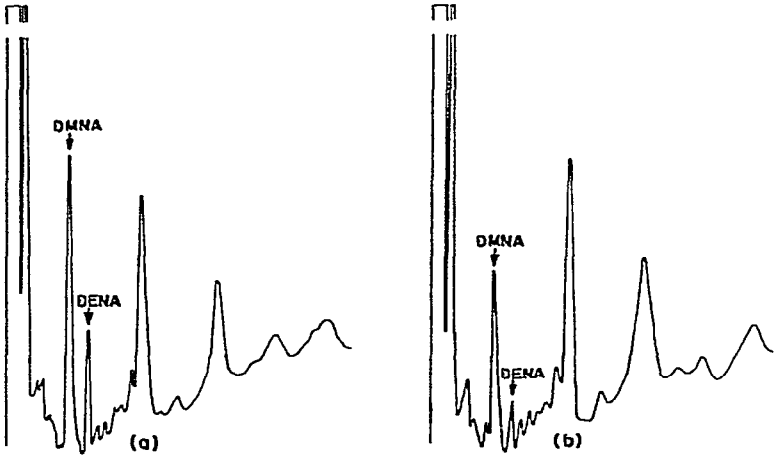


Fig. 6. Cigarette smoke sample: (a) side-stream smoke from four American brand cigarettes irradiated for 60 sec and then "spiked" with a few μl of DMNA–DENA standard (labelled peaks represent 209.7 pg of DMNA and 150.2 pg of DENA); (b) Sample irradiated for 120 sec (labelled peaks represent 106.6 pg of DMNA and 59.3 pg of DENA).

TABLE I

EFFICIENCY OF THE ANALYTICAL PROCEDURE

DMN = dimethylnitrosamine; DMNA = dimethylnitroamine; DEN = diethylnitrosamine; DENA = diethylnitroamine.

| *Amount DMN added (ng)* | *Amount DMNA (ng) (assuming 100% conversion and recovery)* | *Amount DMNA recovered (ng)* | *Recovery (%)* |
|---|---|---|---|
| 65.0 | 79.0 | 28.2 | 36 |
| 65.0 | 79.0 | 35.1 | 44 |
| 65.0 | 79.0 | 27.1 | 34 |
| 130.0 | 158.1 | 47.7 | 30 |
| 130.0 | 158.1 | 53.3 | 34 |
| 130.0 | 158.1 | 60.8 | 38 |
| *Amount DEN added (ng)* | *Amount DENA (ng) (assuming 100% conversion and recovery)* | *Amount DENA recovered (ng)* | *Recovery (%)* |
| 45.5 | 52.6 | 34.3 | 65 |
| 45.5 | 52.6 | 36.5 | 69 |
| 45.5 | 52.6 | 30.8 | 59 |
| 91.0 | 105.3 | 78.4 | 74 |
| 91.0 | 105.3 | 59.1 | 56 |
| 91.0 | 105.3 | 61.1 | 58 |

$3.4 \times 10^{-5}$ sec$^{-1}$ $\pm 0.2 \times 10^{-3}$ sec$^{-1}$ for diethylnitroamine. Fig. 6b shows 7 $\mu$l of the sample after being irradiated for 120 sec. Since the rates of photoreaction of both the "spiked" and "unspiked" samples are within experimental agreement, the presence of dimethylnitroamine in cigarette smoke has been confirmed.

Recovery experiments, which were conducted by adding different amounts of dimethyl- and diethylnitrosamine to 60-ml portions of 1 *N* KOH and carrying out the sample work-up and analyses (as was used for ambient air samples), showed that the average recovery for dimethylnitrosamine is 36%, while that for diethylnitrosamine is 64% (Table I). Preliminary tests indicate that the inclusion of modifications *A* and *B* will lower the recovery by several percent. The experiment conducted to determine the efficiency of the KOH trap[10,18] in retaining dimethyl- and diethylnitrosamine showed that, within the limits of experimental variability (Table I), both compounds appear to have been quantitatively trapped.

The test for artifact formation proved that dimethylnitrosamine was not formed during the cigarette smoke sample collection or work-up via the reaction of nitrite ions (or other nitrosating agents present) with dimethylamine. The two samples collected simultaneously were found to contain the same amount of dimethylnitrosamine, after adjustment for trace levels of dimethylnitrosamine detected in the dimethylamine[20].

## CONCLUSIONS

The analytical procedure presented has been shown to be suitable for detecting sub-ppb levels of volatile nitrosamines in ambient air and cigarette smoke. The lower detection limit for dimethyl- and diethylnitrosamine is *ca.* 0.05 ppb. It is important to note that this procedure contains four tests that must be considered collectively in order to confirm the presence of the nitrosamine(s). These tests are:

(a) Analysis of the sample extract by gas chromatography with an ECD before and after carrying out the oxidation so that the absence of and then appearance of the nitroamine peaks will be observed.

(b) Injection of the oxidized and cleaned-up sample on to two different gas chromatographic columns and then comparing the retention times and peak-height ratios to nitroamine standards.

(c) Irradiation of the resulting nitroamines with UV light and comparing the calculated rates of photoreaction to the constants derived by irradiating nitroamine standards. If the sample contains impurities that affect the rates of photoreaction, as was observed with the cigarette smoke samples, then nitroamine standards can be added to the sample and new matrix-specific photoreaction rate constants can be calculated.

(d) Conducting tests to check for artifact formation.

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