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Note

Photolytic chemiluminescence detector for gas chromatographic analysis of N-nitroso compounds

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N-nitroso compounds are potent environmental carcinogens and their detection is of great interest. Many methods using various chromatographic techniques and detectors have been developed[1,2], the most widely used being the combination of a gas chromatograph with a thermal energy analyzer. The latter is a selective and highly sensitive detector with a detection limit below 100 pg, *e.g.*, 30–40 pg for nitrosodimethylamine[3]. Unfortunately, besides the N-nitroso compounds, this detector also responds to many other compounds like inorganic nitrites and nitrates, some C-nitroso and C-nitro compounds[4]. Therefore, the observation of a positive response does not confirm the presence of an N-nitroso compound, and it has been pointed out that the result obtained with such detector should be confirmed by means of other independent analytical methods[5]. Mass spectrometry (MS) has been recommended for this purpose. However, in many case it cannot be used because of the low concentrations, in which N-nitroso compounds are present in environmental samples[6]. Therefore, approaches based on other chemical or physical techniques have been suggested: they involve treatment with hydrogen bromide in glacial acetic acid or irradiation with UV light[6]. Doerr and Fiddler[7] proposed UV irradiation as a confirmatory method for the presence of nitrosamines.

It is known that N-nitroso compounds are decomposed by UV light[8], releasing nitrosyl radicals, NO$^{\cdot}$. In an aqueous medium NO$^{\cdot}$ is quickly oxidized and hydrolyzed to NO_2^-, which can be quantitatively determined either amperometrically[9] or by means of the Griess reagent. Methods for analysis of nitroso compounds[10,11], including one involving an HPLC detector[12], have been developed on this basis, but their sensitivities are low, *e.g.*, 8–100 ng per injection[12].

In the present paper a new highly selective detection technique is proposed based on the UV decomposition of N-nitroso compounds in the gas phase after their separation by gas chromatography (GC). The NO$^{\cdot}$ radicals thus produced are determined by means of a chemiluminescence detector. The UV photodissociation in the gas phase is expected to have the following advantages compared to that in the liquid phase:

(1) higher quantum yields, because of the absence of a condensed medium

(2) the lifetime of the NO$^{\cdot}$ radicals is greater in the gaseous phase, especially at low concentrations, where the possibility of recombination reactions is reduced.

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EXPERIMENTAL

Apparatus and reagents

A Varian Aerograph 2100 gas chromatograph interfaced with a thermal energy analyzer 502A (Thermoelectron) was used.

A standard solution of seven nitrosamines in ethanol was obtained from Isconlab (Heidelberg, F.R.G.), in the following concentrations: nitrosodimethylamine (NDMA), 0.99 μg/ml; nitrosodiethylamine (NDEA), 0.82 μg/ml; nitrosodipropylamine (NDPA), 0.97 μg/ml; nitrosodibutylamine (NDBA), 0.63 μg/ml; nitrosopiperidine (NPIP), 0.97 μg/ml; nitrosopyrrolidine (NPYR), 1.01 μg/ml; nitrosomorpholine (NMOR), 1.06 μg/ml.

Gas chromatographic conditions: stainless-steel column (3 m × 2 mm I.D.) packed with 15% Carbowax 20M-TPA on Chromosorb W HP (100–120 mesh); carrier gas (argon) flow-rate, 30 ml/min; injection temperature, 210°C; detector temperature, 200°C; oven temperature, 180°C.

A schematic representation of the proposed photolytic chemiluminescence detector is shown in Fig. 1. The outlet (1) of the chromatographic column was connected to quartz tubing (2). (3 mm I.D.) in the form of a coil (15 windings, total length 1 m) wound around a 20-W low-pressure mercury UV lamp (3). In a similar set-up the coil was made of PTFE tubing, but the response decreased rapidly over a short period of time. This was ascribed to cracks allowing passasge of oxygen.

In a second arrangement a 450-W high-pressure mercury UV lamp was used. The quartz coil was placed close to the radiation source in a box the inside of which was covered with aluminium foil.

The time required for passage of the N-nitroso compounds through the coil was calculated to be about 14 s. After the gases have left the coil, they pass through a filter (5) which allows the passage of NO, into the chemiluminescence detector. In our case the latter comprised the reaction chamber of a thermal energy analyzer.

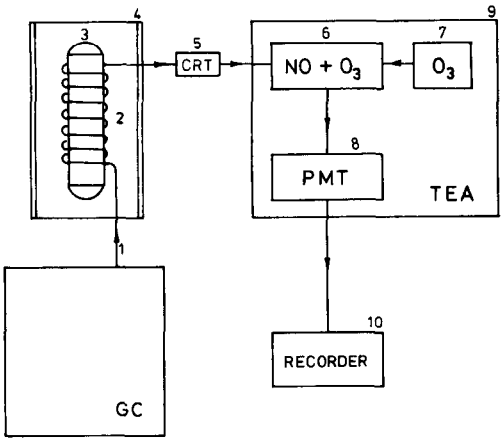

Fig. 1. Schematic representation of the photolytic chemiluminescence detector. 1 = Gas chromatographic outlet; 2 = quartz coil; 3 = UV mercury lamp; 4 = aluminium foil; 5 = gas stream filter (CRT-Thermoelectron); 6 = reaction chamber of thermal energy analyzer; 7 = ozone supply; 8 = photomultiplier tube; 9 = thermal energy analyzer; 10 = recorder.

RESULTS AND DISCUSSION

The basic idea in the present study is to use UV to cleave the N–N bond in N-nitrosyl compounds, forming nitric oxide:

$$R_2N\text{–}N{=}O \xrightarrow{h\nu} R_2N^{\bullet} + {}^{\bullet}N{=}O$$

The NO• is then determined by use of a chemiluminescence detector. Thus after the GC separation of the volatile N-nitrosamines and their photolytical cleavage, a direct response is obtained.

It was interesting to compare the extent of formation of NO• by photodissociation and by the pyrolytic decomposition used in the conventional thermal energy analysis (TEA) procedure. In Fig. 2 typical chromatograms of volatile nitrosamines obtained by UV irradiation (cases A and B, injection volume 5 μl from standard solution) and by the TEA method (case C, injection volume 1 μl from standard solution) are presented. A rather good correlation exists between the two modes of

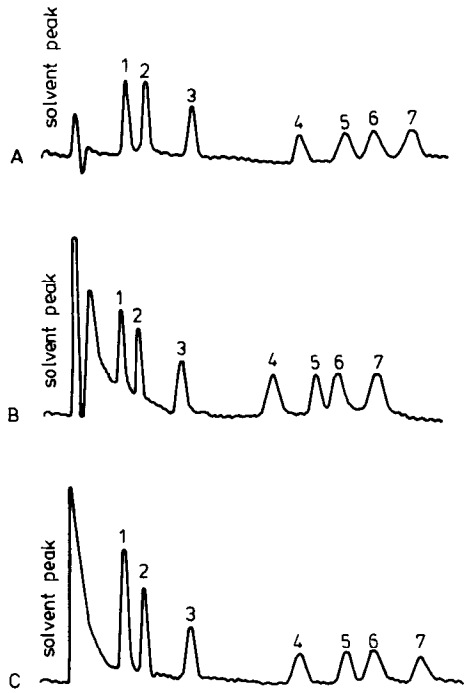

Fig. 2. Comparison between the decomposition of seven nitrosamines upon UV irradiation with low- and high-pressure mercury lamps and upon catalytic pyrolysis at 475°C. (A) Chromatogram obtained after UV irradiation with a low-pressure mercury lamp; injection volume 5 μl of the standard solution. (B) Chromatogram obtained after UV irradiation with a high-pressure mercury lamp; injection volume as in (A). (C) Chromatogram obtained after catalytic pyrolysis at 475°C in the TEA furnace; injection volume 1 μl of the standard solution. Peaks: 1 = NDMA; 2 = NDEA; 3 = NDPA; 4 = NDBA; 5 = NPIP; 6 = NPYR; 7 = NMOR.

nitrosyl radical formation. The sensitivity of the photolytic mode is about five times lower, but it could be increased by prolonging the irradiation time.

The photolytic mode has some advantages compared to the pyrolytic one. According to Krull *et al.*[13], a number of non-nitroso and C,O-nitroso compounds give false positive responses with the standard TEA detector, due to their pyrolytic decomposition. It was shown further that most of these compounds cannot be decomposed by UV light. This fact was used for the development of a more specific method, which includes preliminary UV irradiation followed by TEA. In this connection we consider that the UV irradiation mode is more specific for N-nitroso compounds than the pyrolytic one.

N-nitrosamines have two absorption bands in their UV spectra[14]. The first one at 230–240 nm is intense (ε = 7000 l mol^{-1} cm^{-1}) and is assigned to the $\pi \rightarrow \pi^*$ transition. The second band is of lower intensity (ε = 100) with obvious vibrational structure. It corresponds to the $n \rightarrow \pi^*$ transition and has a maximum at about 350–390 nm.

It was interesting that we obtained almost equivalent results for nitrosyl radical formation using two different mercury lamps, low and high pressure (Fig. 2A and B). Also, that both light sources yield approximately the same quantitative results, which seems to indicate that the irradiation should be preferentially performed at 254 nm.

The proposed technique has a detection limit of 500 pg for NDMA, five to ten times higher compared to TEA. Nevertheless the reported arrangement can be used for environmental analysis, because this sensitivity is enough to detect concentrations at the μg per kg level. Compared to other GC techniques, *e.g.*, with flame ionization detection[15], detection limit 3 ng/μl, the proposed method shows higher sensitivity. The selectivity of the photolytic chemiluminescence detection is also higher. It is known[1] that the most selective GC technique is that employing the Coulson electrolytic conductivity detector. However, with the Coulson detector of the peaks obtained, 50% cannot be confirmed by GC–MS to be N-nitroso compounds.

The proposed detection technique is expected to show better selectivity than TEA. We are now working to improve the sensitivity, by prolonging the irradiation time using a longer quartz tube.

In conclusion, the photolytic chemiluminescence detector can serve as a selective and sensitive technique for the quantitation of N-nitroso compounds.

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