Selective and Sensitive Determination of *N*-Nitrosamines in Environments by Gas Chromatography with Flame Photometric Detection

HIROYUKI KATAOKA, SEIKO SHINDO, MARI KURISU and MASAMI MAKITA

Faculty of Pharmaceutical Sciences, Okayama University, 1-1-1 Tsushima-naka,
Okayama 700, Japan

Introduction

N-Nitrosamines, potent mutagenic and carcinogenic compounds, are widely distributed in various human environments. In the present study, we investigated a selective and sensitive method for the determination of *N*-nitrosamines, based on their denitrosation to secondary amines, subsequent conversion of secondary amines into *N*-diethylthiophosphoryl (DETP) derivatives and gas chromatography with flame photometric detection (GC-FPD).¹⁾ This method was used to determine *N*-nitrosamines in combustion smoke samples.

Methods

Smoke was bubbled in 5% HCl containing 20 mM ascorbic acid using a laboratory-made smoking machine. The smoke sample was extracted twice with diethyl ether containing 25% isopropanol. After evaporation to dryness of the solvent, HBr was added to the residue and the tube was heated for 5 min at 100°C while tightly capped. After neutralization with NaOH solution, 0.2 ml of 1% diethylchlorothiophosphate and 0.2 ml of 10% Na₂CO₃ were added to the mixture, then it was heated at 60°C for 10 min while tightly capped. The reaction mixture was heated again to remove the excess reagent after addition of cysteic acid solution; it was then extracted with 0.2–0.4 ml of *n*-hexane and 1 µl of this extract was injected into the GC-FPD.

Results and Discussion

The denitrosation of *N*-nitrosamines with HBr proceeded rapidly and quantitatively. The resulting secondary amines could be conveniently

converted into their *N*-DETP derivatives by the previously reported method.^{2,3)} The derivatives provided an excellent response in the FPD, and the calibration curve for each *N*-nitrosamine in the range 0.05–1 nmol was linear and sufficiently reproducible for quantitative determination.

This method was successfully applied to smoke samples without prior clean-up and *N*-nitrosamines in these samples were determined without any interference from coexisting substances. *N*-Nitrosamines and secondary amines in the samples were completely separated by extraction with diethyl ether containing 25% isopropanol. Overall recoveries of *N*-nitrosamines added to cigarette smoke were 83–110%. *N*-Nitrosodimethylamine (NDMA), *N*-nitrosopyrrolidine (NPYR) and *N*-nitrosopiperidine (NPIP) were detected in the smoke. The *N*-nitrosamine contents in sidestream smoke was 2–6 times higher than that in mainstream smoke. Most of these *N*-nitrosamines were found to be formed during the combustion of the cigarette. The smoke of black pepper and dried squid contained high concentrations of NDMA, NPYR and NPIP, while a high concentration of *N*-nitrosomorpholine was detected in rubber smoke. These results suggest there is a cancer risk due to exposure to these various types of combustion smoke which can occur in human environments.

References

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