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CHEMILUMINESCENT NITROGEN DETECTOR–GAS CHROMATOGRAPHY AND ITS APPLICATION TO MEASUREMENT OF ATMOSPHERIC AMMONIA AND AMINES

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SUMMARY

A nitrogen-sensitive detector for gas chromatography was constructed by utilizing a commercial chemiluminescent nitrogen oxide analyser in conjunction with formation of nitrogen monoxide from nitrogen-containing compounds by pyrolysis on the hot platinum catalyst. The detector is very specific and quite sensitive to nitrogen compounds. There is no interference from other hydrocarbons. The collection ability of the adsorbents for ammonia and amines was determined in terms of (1) breakthrough volume and/or (2) collection efficiency. The maximum loading capacities of the adsorbents are 3.0 $\mu g/g$ for ammonia on alkalized Porasil A, more than 2 $\mu g/g$ for amines on all adsorbents studied. The recoveries of adsorbed compounds were measured by gas chromatographic analysis after thermal injection and almost 100% of ammonia and amines were recovered from Tenax-GC and alkalized Porasil A, but less quantitative from Porapak T and Chromosorb T. The present method was successfully applied for a determination of atmospheric ammonia and trimethylamine.

INTRODUCTION

In order to determine minor constituents in air, they have to be pre-concentrated by a proper collection method. Ambient temperature adsorption and thermal desorption techniques have advantages over collection on a filter paper or in solution, such as (i) no reagent blank, (ii) an ease of handling, and (iii) small sample size due to injection of whole amounts collected to gas chromatography. Ambient temperature collection of ammonia and amines is not get popular[1,2], though they are one of the major nuisances as offensive odour. This is because of severe interference from hydrocarbons in gas chromatography with a flame ionization detector (GC–FID), the detection is not selective to nitrogen compounds. In order to avoid this problem, the selective detector must be used.

Recently, the performance of the flame thermionic detector (FTD) which is very specific to nitrogen and phosphorus compounds has been improved sufficiently to detect picogram levels of these compounds[3]. Chemiluminescence from a reaction

between nitrogen monoxide and ozone can be also used for specific detection of N-nitrosamines after thermal cleavage of N–NO bond, and a detector based on this principle is called a thermal energy analyser (TEA)[4].

We constructed a nitrogen-selective detector by employing a commercial nitrogen oxide analyser in conjunction with pyrolysis of nitrogen-containing compounds[5], and applied gas chromatography with a chemiluminescent nitrogen detector (GC–CLD) for measurement of ammonia[6] and trimethylamine (TMA)[7] in air. The present paper deals with the performance of the chemiluminescent nitrogen detector and the adsorption behaviour of ammonia and amines to some adsorbents.

EXPERIMENTAL

Apparatus

The GC–CLD system consisted of a chromatograph, a pyrolyser, and a CL-NO_x analyser (Fig. 1). A Shimadzu 4BM-GC chromatograph was used, and a column separation was done with a glass column (3m × 3 mm I.D.) packed with either 5% squalane + 2% KOH on Chromosorb 104 (80–100 mesh) or on Chromosorb 103 (80–100 mesh) isothermally at 130°C with nitrogen carrier gas at a flow-rate of 50 ml/min. The pyrolyser was a quartz tube (20 cm × 6 mm I.D.) packed with platinum net in 10 cm long heated at 900°C, and the detector was a chemiluminescent nitrogen oxide analyser (Bendix Model 8101-C) with 0.5, 1.0, and 2.0 ppm full scale range.
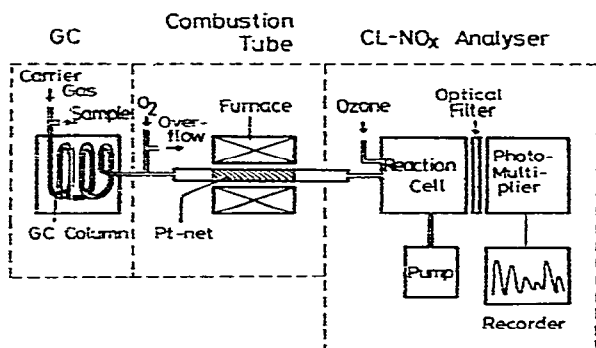

Fig. 1. Schematic view of GC–CLD.

Materials

Standard solutions for ammonia, methylamine (MMA), dimethylamine (DMA), and TMA were prepared by diluting aqueous solutions (30%) of each compound (Wako, Osaka, Japan, "S" grade) with water and standardized by the titrimetric method with hydrochloric acid.

Standard gases for each compound were made by vapourizing *ca.* 1 μl of aqueous solution in a nitrogen-filled sampling bottle (1 l) and further diluted with nitrogen gas in another bottle (DMA). Its concentration was calibrated with the standard solution by GC. The sample gas stream with a constant concentration at ppb*levels was prepared by diluting a vapour permeating through a permeation tube

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* Throughout this article, the American billion (10^9) is meant.

wall with air compressed from a laboratory room with an air pump. The dilutant air was desiccated with silica gel but not purified further. The permeation tube was prepared by filling concentrated aqueous solution for each compound, instead of liquefied gas[8], into a PTFE tube (FEP, 4 cm × 7 mm O.D. × 6 mm I.D.) with both ends plugged with glass stoppers[9]. The concentration of the diluted sample gas was determined either by colorimetry or by GC after collection in an acidic solution.

The collection tubes for Porapak T, Chromosorb T, and Porasil A were of glass (10 cm × 6 mm I.D.), and the tube for Tenax-GC was longer (18 cm). One end of the tube was plugged with silicone rubber and the other was attached to a syringe needle. Porasil A was coated with 5% KOH. They were conditioned according to refs. 2 and 10.

RESULTS AND DISCUSSION

Response of the chemiluminescent nitrogen detector to nitrogen compounds

The chemiluminescent nitrogen oxide analyser is based on measurement of the light emitted by the relaxation of excited-state NO_2^*, which is produced in a reaction of nitrogen monoxide with ozone, to ground-state NO_2. Therfore, the sensitivity of CLD towards nitrogen compounds is governed by the effectiveness of the conversion from nitrogen compounds into nitrogen monoxide. Nitrogen-containing compounds decompose stoichiometrically to yield NO by combustion in an oxygen stream with a proper catalyst[11].

The response of nitrogen compounds to the CLD was measured by injecting *ca.* 40 ng of each compound into a pyrolyser directly without a column separation. The result is shown in Fig. 2, in which the ordinate is the intensity of nitrogen monoxide on the CLD and the abscissa represents the number of moles corresponding to 10 ng for each compound. From Fig. 2 it is clear that the CLD has a good response to nitrogen compounds. Particularly ammonia, acetonitrile and nitromethane have a higher sensitivity than amines by a factor of *ca.* 1.5.

Raising the temperature of the pyrolyser gave a steady increase of CLD signal up to 900°C. A peak height at 500°C is *ca.* 80% of that at 900°C with a large peak
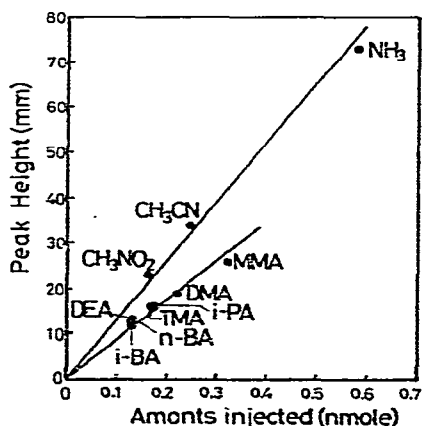

Fig. 2. Response of the CLD to various nitrogen compounds.

tailing. There is no significant interference from other hydrocarbons, and 1 μl of solvents such as ethanol, acetone, hexane, benzene gave a small peak equivalent to a new nanograms of TMA. As shown in Fig. 3, with GC–CLD it is possible to determine even diethylamine (DEA), which is hidden in the solvent peak in GC–FID.
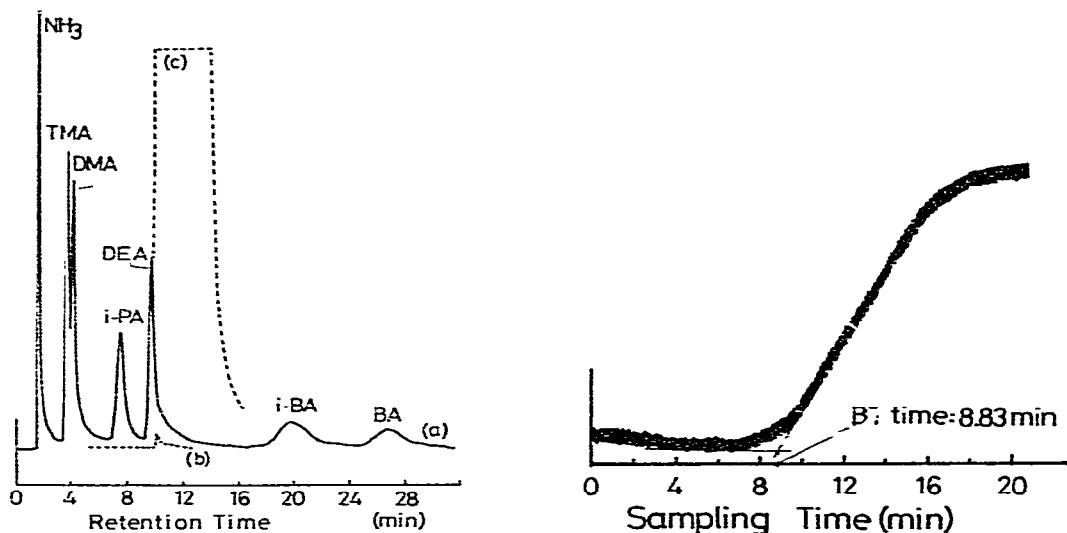

Fig. 3. Gas chromatogram of amines with GC–CLD. Conditions: 5% squalane plus 2% KOH/Chromosorb 104 (80–100 mesh) in a glass column (2 m × 3 mm I.D.), isothermally at 130°C with nitrogen flow-rate of 60 ml/min. (a) Mixed standard sample in ethanol solution. (b) Ethanol only. (c) Ethanol with GC–FID.

Fig. 4. Break-through curve of TMA (0.28 ppm) on Chromosorb T sampled with 0.6 l/min at 18°C.

Collection capacity of adsorbent tube

The collection tube must have a large capacity at ambient temperature (large adsorbing constant). The capacity of the collection tubes was measured by two methods: (1) from the collection efficiency and (2) from the breakthrough volume. The collection efficiency of the adsorbent was measured by either connecting two collection tubes in series or using a cryogenic trap as the backup. Measurements were carried out by sampling the sample gas in low concentrations through the adsorbent tube by the air pump. Results for TMA with Tenax-GC are shown as a function of sampling rate in Table I. For ammonia with alkalized Porasil A, no ammonia was observed in the backup tube at flow-rates of up to 0.8 l/min, indicating almost 100% collection efficiency for the front tube.

The breakthrough volume was determined by drawing the sample gas through the collection tube in a thermostat with a fixed sampling rate. A fraction (about 100 ml/min) of the exit air stream from the tube was monitored continuously by CLD without a column separation. A typical breakthrough curve is shown in Fig. 4. The breakthrough volume was calculated from the breakthrough time of the signal multiplied by the fixed sampling rate at the given temperature. The change in breakthrough volume as a function of temperature is shown in Fig. 5 for ammonia and in Fig. 6 for TMA*.

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* Similar behaviours to TMA were also obtained for DMA and MMA.

TABLE I

COLLECTION EFFICIENCY OF TMA WITH TENAX-GC AT 20°C

Sampling rate (l/min)	Collection efficiency (%)
0.29	100
0.54	100
0.78	90.1
1.05	93.8
1.41	88.4

The variation of breakthrough volumes with temperature follows two different curves, a steep line at higher temperatures and nearly constant value at lower collection temperatures. The line at high temperatures is insensitive to the concentration of sample gas, and all amines lie on almost the same line for a given adsorbent. This indicates that retention volume is dependent on temperature[12], and also a tendency to thermal release and easier desorption by heating. On the other hand, the constant line at lower temperatures went up and down depending on the gas concentration. However, almost constant values were obtained by multipling the gas concentration by the breakthrough volume. This is the maximum amount of substance that can be adsorbed on the given adsorbent and is called the maximum loading capacity (^mL_c) of the adsorbent. For ammonia no distinct saturation was observed at lower temperatures. This may be due to very fast transfer of ammonia through the tube, as observed by McClenny[1].
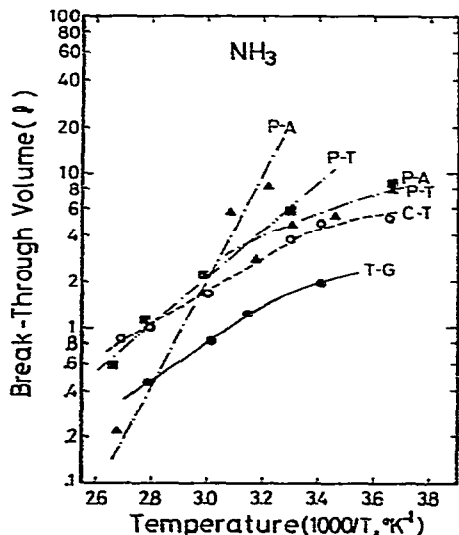

Fig. 5. Temperature dependence of breakthrough volumes for ammonia with adsorbents used. ●—●, Tenax-GC (0.3 ppm); ■—■, Porapak T (0.3 ppm); O—O, Chromosorb T (0.2 ppm); ▲—▲, Porasil A (ca. 1 ppm).
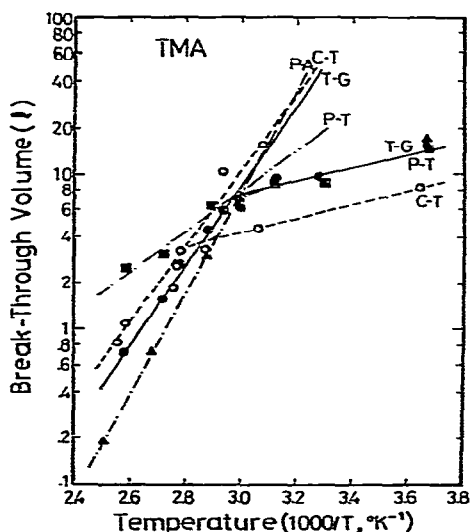
Fig. 6. Temperature dependence of breakthrough volumes for TMA with adsorbents used. ●—●, Tenax-GC (0.10 ppm); ■—■, Porapak T (0.13 ppm); O—O, Chromosorb T (0.18 ppm); ▲—▲, Porasil A (> 2 ppm).

Table II shows the maximum loading capacities of adsorbents used for ammonia and amines at 18°C. For alkalized Porasil A, the breakthrough phenomena could not observed after passage of 60 l of the sample gas (2 ppm), but a strong odour was detected and a very large peak of TMA was obtained by injection on to the gas chromatograph.

TABLE II

MAXIMUM LOADINGS CAPACITIES (^mL_c) OF ADSORBENTS USED AT 18°C

Adsorbent	Amounts packed (g)	^mL_c (µg/g)			
		NH_3	MMA	DMA	TMA
Tenax-GC	0.6	0.7	3.2	5.7	4.5
Porapak T	0.8	2.1	3.6	8.4	4.8
Chromosorb T	0.9	0.6	>2	4.7	4.0
Porasil A	1.0	3.0			>18

From Table II, Porapak T and alkalized Porasil A have a sufficiently large capacity to adsorb both ammonia and amines in air. Chromosorb T and Tenax-GC can also be used as adsorbent for amines at low ppb levels. By stepwise sampling of the gas in a low concentration with Tenax-GC, the amount of TMA was determined by GC–FID and the corresponding concentrations of the gas were calculated for each measurement. From the results shown in Fig. 7 along with the breakthrough curve for the gas it can be concluded that the maximum sampling volume is ca. 1.5 times larger than the breakthrough volume for the same gas. This indicates that the breakthrough volume can be used as a measure of the sample size for each adsorbent tube.

Recovery of adsorbates from adsorbents

A good collection tube for GC must have not only a large collection capacity but also a quantitative recovery of adsorbates by thermal desorption. The recovery of ammonia and amines from the collection tube was measured with the standard gases and was almost 100% for TMA from Tenax-GC[7] and ammonia[6] and DMA from alkalized Porasil A.

Porapak T and Chromosorb T gave a poor recovery due to the low temperature allowable, particularly for DMA. Overall recovery for the whole procedure was

TABLE III

RECOVERIES OF ADSORBATES FROM COLLECTION TUBE WITH 8 l OF THE MIXED GAS

Adsorbent	Recoveries (%)		
	NH_3 (130 ppb)	DMA (70 ppb)	TMA (23 ppb)
Tenax-GC	20.0	80.3	100*
Porasil A	100*	100*	104.6
Chromosorb T	91	74.2	85.2
Porapak T	—	—	76.3

measured by sampling 8 l of a mixed gas at ppb level with the collection tube. The results shown in Table III are expressed by comparing the values to those marked (*) which were considered as 100 %. It was not possible to achieve a satisfactory recovery for ammonia and DMA from Porapak T. Recovery of MMA was not reproducible, even with the standard gas.

Application

We applied ambient temperature preconcentration and GC–CLD to the determination of atmospheric ammonia and amines. TMA in freezer air was analysed with GC–CLD after preconcentration with a Tenax-GC tube. The gas chromatogram for 6 l of the freezer air is shown in Fig. 8, and the amount of TMA was 35 ng, corresponding to 2.4 ppb, whereas a 0.1 N H_2SO_4 collection cryogenic trap and GC–FID gave 5.8 ppb and 1.3 ppb with 15 l of the same gas. Both results can be said to be in relatively good agreement.
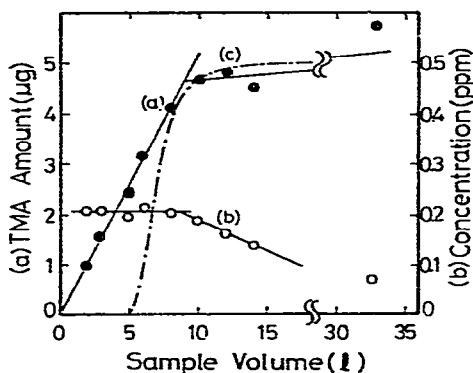

Fig. 7. Relation between TMA amounts collected and sample volumes with Tenax-GC at 22°C. (a) ●—●, Amount of TMA collected; (b) ○—○, TMA concentration; (c) break-through curve.
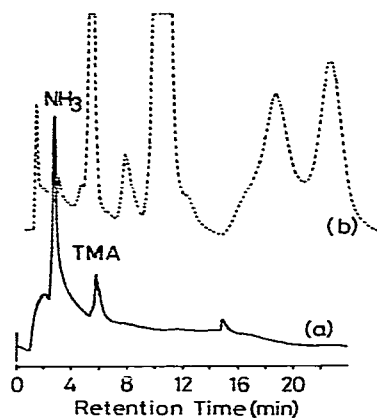
Fig. 8. Gas chromatogram of 6 l of freezer air with Tenax-GC: (a) GC–CLD; (b) GC–FID. GC conditions as in Fig. 3.

Ammonia in air around the boundary zone of a cattle farm was also measured by collecting with alkalized Porasil A, and 129 ppb was obtained with 0.4 l of sample gas.

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