

Short Communication

Flame-photometric detection of nitrous oxide in addition to phosphine

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ABSTRACT

Nitrous oxide can be separated from phosphine in a short (10 m) capillary column coated with a porous layer of Porapak Q, and determined under phosphorus-sensitive flame-photometric detection (P-FPD) conditions at 526 nm. The detection limits of nitrous oxide depend on the detector gas flows. A high oxygen/hydrogen ratio (0.8) is favourable to the nitrous oxide determination with a detection limit of $20 \cdot 10^{-12} \text{ m}^3$. The specificity of P-FPD remains at the 100:1 ratio in favour of phosphine.

INTRODUCTION

During experiments aimed at detecting traces of phosphine in marine sediments by gas chromatographic (GC) separation and flame-photometric detection (FPD), nitrous oxide gave positive detector responses under phosphorus-selective conditions. These very disturbing results caused us to investigate in more detail the detectability of nitrous oxide by phosphorus-selective FPD (P-FPD), since the specific detection of nitrous oxide under phosphorus-selective conditions was hitherto unknown. Generally, nitrogen-containing compounds show a weak emission of NH_2 bands between 440 and 700 nm and of CN bands between 385 and 388 nm [1] (see also ref. 2).

Nitrous oxide is a conservative constituent of the atmosphere. The ambient concentration is about $300 \text{ mm}^3 \text{ m}^{-3}$. The most sensitive method of detect-

ing nitrous oxide involves high-temperature electron capture detection [3,4]. The detection limit is about $10 \cdot 10^{-15} \text{ m}^3$. Phosphine, used in the food industry and by electronic chip manufacturers as a fumigant and as a dopant, respectively, can be selectively detected by flame photometry [5,6] at a wavelength of 526 nm with a detection limit of $0.5 \cdot 10^{-15} - 1 \cdot 10^{-15} \text{ m}^3$.

MATERIALS AND METHODS

Phosphine (0.5%, v/v) in nitrogen and nitrous oxide were obtained from Messer-Griesheim. A Carlo Erba GC 2900 gas chromatograph equipped with a phosphorus (526 nm) flame photometric detector (Model SSD-250) and a Hitachi-Merck recording integrator (Model D-2500) were used. The gaseous samples were introduced from a pressurized 1-dm^3 glass flask through a fused-silica capil-

lary trap (3 m × 0.1 mm) cooled with liquid nitrogen into a capillary column (Chrompack Poraplot Q, 10 m × 0.32 mm × 10 μm). The sample gas flow and volume were measured by a flow meter and a gas burette connected between the capillary trap and analytical column by a three-way capillary valve (Gerstel GC 02943-31). The GC conditions were: carrier gas, hydrogen; pressure, 10⁵ Pa (2.8 cm³ min⁻¹); oven temperature, 313 K, detector temperature, 448 K; detector gases, hydrogen 0.8 · 10⁵–1.3 · 10⁵ Pa (20–45 cm³ min⁻¹), air 2.5 · 10⁵–3.5 · 10⁵ Pa (90–130 cm³ min⁻¹).

RESULTS

Two sets of experiments with constant chromatographic but variable detector conditions were carried out. For the first set (indicated by a Roman numeral I in Fig. 1) we chose a detector gas flow of hydrogen (20 cm³ min⁻¹) and air (90 cm³ min⁻¹) just at the point where the flame would be extinguished by increasing air flow or decreasing hydrogen flow. These were very unfavourable conditions for the detection of phosphorus compounds. Therefore, phosphine can only be detected in the 200 ·

10⁻¹⁵–600 · 10⁻¹⁵ m³ range. For the detection of nitrous oxide, these gas flows are highly favourable. Nitrous oxide can be detected in the 20 · 10⁻¹²–400 · 10⁻¹² m³ range (see also Fig. 2). The detection limit for phosphine is 200 · 10⁻¹⁵ m³ and for nitrous oxide 20 · 10⁻¹² m³. Obviously, the specificity of the detector remains at the 100:1 ratio in favour of the phosphorus compound at the detection limits.

In the second set of experiments (indicated by the Roman numeral II in Fig. 1), the detector gas flows (45 cm³ min⁻¹ for hydrogen and 130 cm³ min⁻¹ for air) were increased in order to establish a level of flame stability whereby small changes in both flows would not significantly change the detector signal. The detection of phosphine increases drastically (to the 5 · 10⁻¹⁵–100 · 10⁻¹⁵ m³ range), while the detector response of nitrous oxide turns out to be ambiguous. The detector response for higher mass flows increases while lower mass flows are less detectable. The detection limit for phosphine in this case was 5 · 10⁻¹⁵ m³ and for nitrous oxide 100 · 10⁻¹² m³. The detector specificity for phosphorus over nitrous oxide turns in favour of phosphine to 20 000:1.

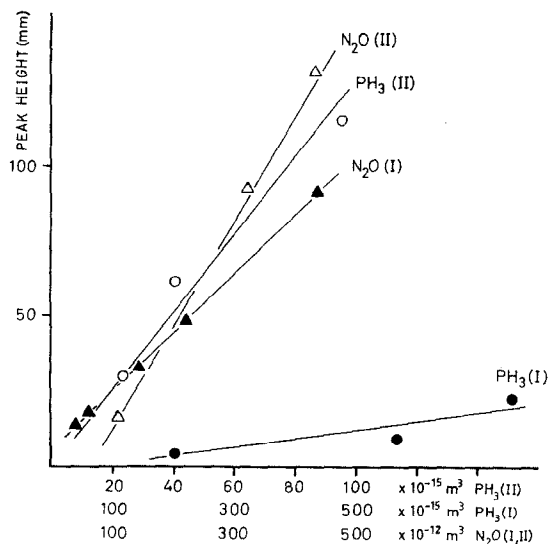


Fig. 1. Peak heights versus different amounts of nitrous oxide (N₂O) and phosphine (pH 3) depending on detector gas flows: I = 20 cm³ min⁻¹ hydrogen and 90 cm³ min⁻¹ air; II = 45 cm³ min⁻¹ hydrogen and 130 cm³ min⁻¹ air.

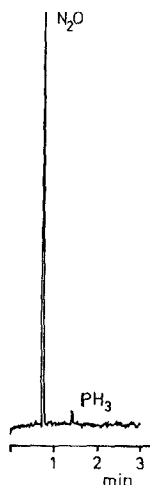


Fig. 2. Nitrous oxide (540 · 10⁻¹² m³) and phosphine (275 · 10⁻¹⁵ m³) separated on a Poraplot Q capillary column (10 m × 0.32 mm × 10 μm) and detected by P-FPD with detector gas flows of 20 cm³ min⁻¹ hydrogen and 90 cm³ min⁻¹ air.

DISCUSSION

The detection limits of phosphine and nitrous oxide shown in these experiments are not at all impressive. Other flame photometric detectors exhibit a much better performance for the detection of phosphine. FPD of nitrous oxide is 2000 times less sensitive than electron-capture detection. Nevertheless, it is very disturbing that nitrous oxide may interfere with the phosphine determination in cases where a complete chromatographic separation has not been achieved. In such cases, the presence of a phosphorus compound might be presumed where in fact only higher levels of nitrous oxide are present. As the discussion on the presence or absence of phosphine in nature has intensified [7], the demonstration of a positive P-FPD response to nitrous oxide shows that the interpretation of this signal as "phosphorus"-containing or even as "phosphine" must be regarded with caution.

ACKNOWLEDGEMENTS

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