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DETECTION OF INORGANIC GASES USING A FLAME IONISATION DETECTOR

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SUMMARY

A flame ionisation detector has been used for the detection of some inorganic gases. The use of a hydrogen-rich flame with oxygen to support combustion resulted in a significant response towards a number of inorganic gases. Conditions for optimum response are given and a table of response data and detection limits is presented. The response of the detector is highest toward nitric oxide and is the same as that observed for methane.

INTRODUCTION

The separation of inorganic gases and light hydrocarbons by gas chromatography (GC) is well established and many papers have been published describing suitable columns and operating conditions. The majority of workers use porous polymer bead¹⁻³ and molecular sieve columns⁴⁻⁶. The most frequently used detector for inorganic gases is the katharometer, and for hydrocarbons the flame ionisation detector (FID). Detection limits for permanent gases using the katharometer vary considerably with cell design. For most gases limits are in the region of 100 $\mu\text{l/l}$, but a limit of 20 $\mu\text{l/l}$ for carbon dioxide⁷ has been reported. It is recognised that under conventional operating conditions the FID has a negligible response to inorganic gases⁸⁻¹¹. The introduction of a continuous supply of methane into the flame to enhance the standing current has been used by Garzo and Fritz¹² in order to selectively detect silicon containing compounds. Other workers¹³⁻¹⁵ have used this technique and have found that under carefully selected conditions the FID will respond to some inorganic gases. Askew¹⁶ used fluorinated hydrocarbons as the ionising gases and obtained enhanced responses towards nitrogen, helium, carbon dioxide and sulphur dioxide. Detection limits have been calculated from the data presented in these papers and are given for comparative purposes in Table I. The electron capture detector is of little value for inorganic gas detection, but has been used for the oxides of nitrogen down to 10 $\mu\text{l/l}$ ¹⁷.

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TABLE I
COMPARISON OF DETECTION LIMITS

Gas	Detection limit (g/sec)		
	Methane FID*	Flame emission**	Dielectric constant***
Ar	not tested	3×10^{-7}	8×10^{-8}
CH ₄	2×10^{-11}	not tested	2×10^{-10}
CO	4×10^{-7}	not applicable	6×10^{-10}
CO ₂	4×10^{-7}	1×10^{-6}	9×10^{-10}
He	7×10^{-8}	6×10^{-7}	not tested
H ₂ S	1×10^{-8}	not tested	not tested
NO	2×10^{-8}	not tested	not tested
N ₂	1×10^{-6}	8×10^{-7}	6×10^{-10}
N ₂ O	5×10^{-8}	1×10^{-6}	2×10^{-10}
NO ₂	not tested	not tested	2×10^{-10}
O ₂	7×10^{-8}	4×10^{-7}	6×10^{-10}
SO ₂	7×10^{-8}	not applicable	3×10^{-10}

* Calculated from data in references 10 and 13-16, assuming a noise level of 1×10^{-13} A.

** Ref. 19.

*** Ref. 20.

Several less well-known detectors have been used for permanent gas analysis, most of which are not commercially available. By far the most sensitive is the helium ionisation detector which gives limits in the nl/l range¹⁸. The flame emission¹⁹ and dielectric constant²⁰ detectors both respond to inorganic gases (*cf.* Table I). A palladium-silver alloy tube acting as a transmodulator has been used in conjunction with a katharometer to effectively increase its sensitivity by up to three orders of magnitude for the detection of the rare gases²¹. The present work describes some experiments carried out using a commercially available FID with a view to obtaining better detection limits than those previously obtained by flame detection.

EXPERIMENTAL

A Pye 104 gas chromatograph fitted with a normal FID was used. Gas samples were introduced on to a Porapak Q column by means of a sampling valve and 1-ml capacity loop connected directly to a sample gas reservoir. Dilute gas samples were prepared by injecting known volumes of the pure gas under study into an evacuated cylinder, which was then charged with the diluent gas to the appropriate pressure. The diluent gas was the same as the carrier gas.

RESULTS AND DISCUSSION

Initial experiments using a methane-argon (1:9) mixture, hydrogen and air for combustion gave detection limits for nitric oxide similar to those reported by Schaefer¹⁵ for other inorganic gases, using standing currents up to 1×10^{-7} A. The main limitation to improving detection limits was clearly the high noise level of the system. In the absence of methane the noise was that of a conventional flame (5×10^{-14} A). It was observed that a higher than normal standing current could be obtain-

ed without a corresponding increase in noise, when the ratio of hydrogen to air flow-rates at the detector was increased. This also gave rise to a finite response for nitric oxide. Further substantial increases in response were obtained when oxygen was used in place of air, and a less noisy flame was obtained when pure hydrogen was used in place of commercial grade, and nitrogen instead of argon used as carrier gas. All gases were filtered and passed through molecular sieve and activated charcoal. With the hydrogen-rich flame an excessive amount of condensed water vapour gave rise to a drastic increase in noise after operating for a short period. This was eliminated by operating the detector without its top cap. Increasing the temperature of the detector body, although minimising condensation, resulted in a permanent increase in noise.

Further improvements in performance were achieved by incorporating 1-mm diameter holes in the collector electrode near its base. Using nitric oxide the optimum response of the detector was found by varying in turn the carrier gas, hydrogen and oxygen flow-rates. The flow-rates were interdependent and Fig. 1 shows the effect of varying each gas in turn with the remaining gas flows set in the region for optimum response. These data were derived from 1-ml injections of a 250- μ l/l mixture of nitric oxide in nitrogen. Conditions for optimum response for nitric oxide were reproducible from day to day and were in the range of 15–30 ml/min carrier gas, 60–70 ml/min hydrogen and 35–45 ml/min oxygen. A chromatogram showing the response to 5 μ l/l of nitric oxide is shown in Fig. 2. Reproducibility of response, measured over 10 replicate injections of this mixture was satisfactory. The variation of standing current with changes in flow-rate is given in Fig. 3. The response of the detector was found to be linear over the whole range studied (1–1000 μ l/l) and this is shown in Fig. 4. A

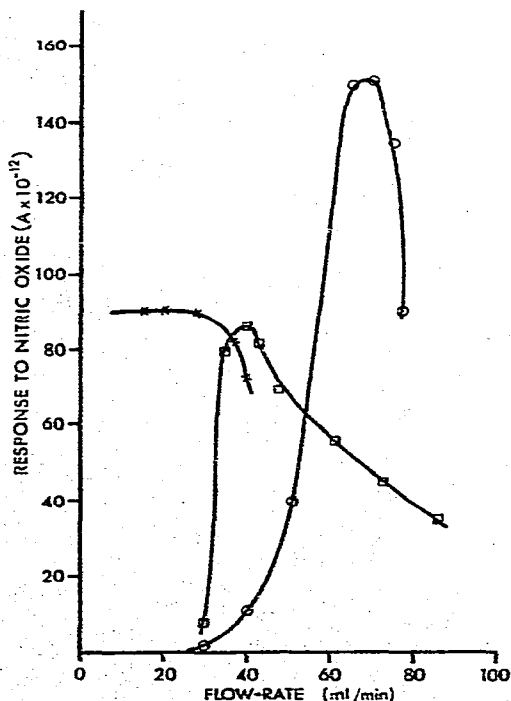


Fig. 1. Effect of gas flow-rates on detector response. \times , Nitrogen, \circ , hydrogen; \square , oxygen.

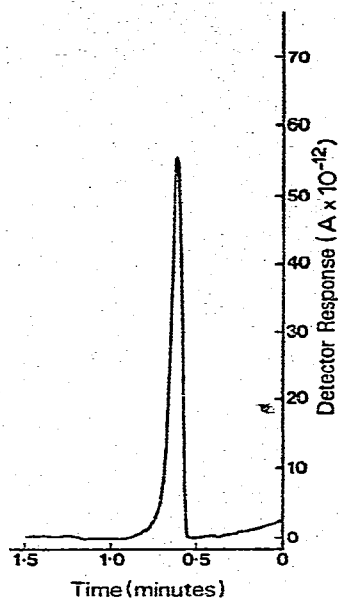


Fig. 2. Chromatogram of a 1-ml sample of 5 μ l/l nitric oxide in nitrogen.

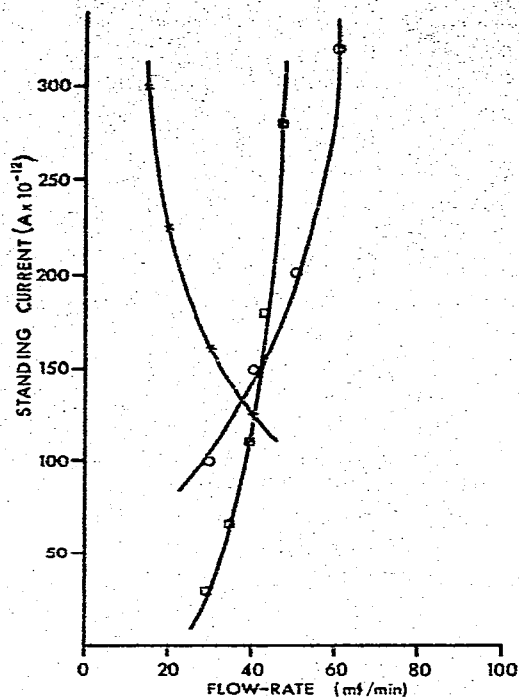


Fig. 3. Effect of gas flow-rates on standing current. \times , Nitrogen; \circ , hydrogen; \square , oxygen.

summary of the characteristics of the detector operating in the hydrogen-rich mode is given in Table II.

The noise level compares favourably with that of a conventionally operated FID and the detection limit for nitric oxide is three orders of magnitude better than previously published data (*cf.* Tables I and II). Its response (C/g) is the same as that for a hydrocarbon using a normal flame. Confirmation that the nitric oxide itself and not a reaction product derived from nitric oxide and the column²² was entering the flame was made by combined GC and mass spectrometry using the same GC system. Nitric oxide was detected in the mass spectrometer using Porapak and Carbowax 20M columns and both stainless-steel and glass column tubing. The only impurities observed were sulphur dioxide, carbonyl sulphide, carbon dioxide, oxygen and water vapour. The sulphur compounds were present at less than 0.3%, and there was no detectable increase in the background levels of the remaining gases in the mass spectrometer when the nitric oxide was introduced. In any case all the above gases would be resolved from nitric oxide by Porapak Q and would not therefore enhance any response due to nitric oxide.

Under optimum conditions for nitric oxide, the response of the detector to some other inorganic gases was measured and these are listed in Table III. Conditions for optimum response for carbon monoxide, carbon dioxide, sulphur dioxide and hydrogen sulphide were sought using the same procedure described for nitric oxide. No substantial improvement in response could be obtained over those values determined under optimum nitric oxide response conditions. Changes in carrier gas flow-rate to obtain reasonable retention times could be accommodated without detriment to the response, provided the fuel gas flow-rates were also changed to maintain a constant

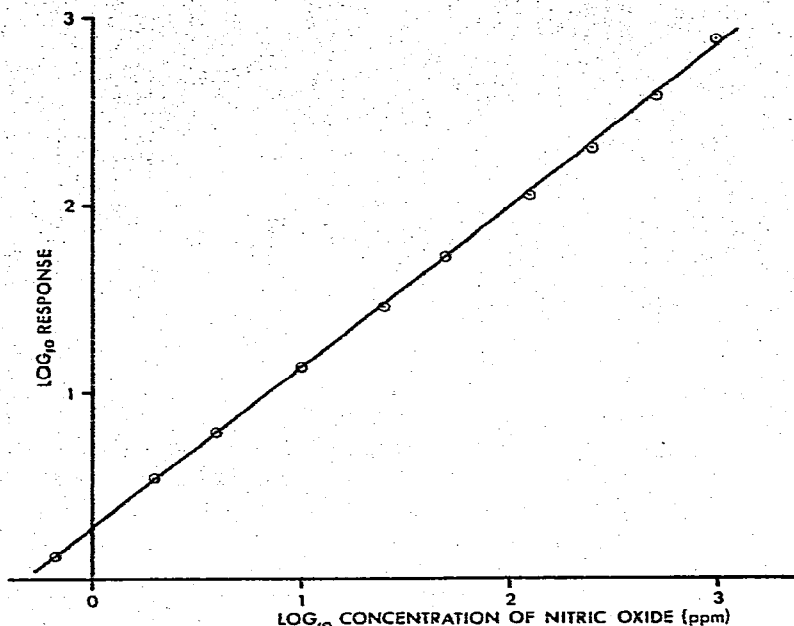


Fig. 4. Linearity of response to nitric oxide.

TABLE II

HYDROGEN-RICH FID OPTIMISED FOR NITRIC OXIDE DETECTION

<i>Parameter</i>	<i>Value</i>
Noise level	1×10^{-13} A
Standing current	2×10^{-10} A
Response	1×10^{-3} C/g
Detection limit	2×10^{-11} g/sec
Reproducibility of response	0.6%
Linear dynamic range	$> 10^3$

TABLE III

RESPONSE DATA FOR THE HYDROGEN-RICH FID

<i>Gas</i>	<i>Response (C/g)</i>	<i>Detection limit (g/sec)</i>
Ar	3×10^{-8}	7×10^{-6}
CH ₄	1×10^{-2}	2×10^{-11}
CO	2×10^{-6}	1×10^{-7}
CO ₂	5×10^{-6}	4×10^{-8}
He	4×10^{-6}	5×10^{-8}
H ₂ S	5×10^{-4}	4×10^{-10}
NO	1×10^{-2}	2×10^{-11}
N ₂ O	3×10^{-5}	7×10^{-9}
NO ₂	1×10^{-4}	2×10^{-9}
O ₂	4×10^{-6}	5×10^{-8}
SO ₂	5×10^{-4}	4×10^{-10}

ratio between the various gases, and the standing currents were between 1 and 5×10^{-10} A.

Comparison between Tables I and III shows that for all the gases listed the hydrogen-rich FID has a detection limit at least as low as other flame detectors. For hydrogen sulphide and sulphur dioxide it is two orders of magnitude lower and for nitric oxide three orders of magnitude.

The application of this work to the detection of nitrosamines as nitric oxide has been described elsewhere²³ and a comparison of the hydrogen-rich FID with various other methods of detection for nitric oxide has been made²⁴. Further work on this mode of detection is in progress.

CONCLUSIONS

With minor modifications a commercially available FID can be used to detect small concentrations of a variety of inorganic gases. Detection limits compare favourably with other normally available detectors and for some gases an improvement of several orders of magnitude is obtained.

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