*Journal of Chromatography*, 178 (1979) 364–368


CHROM. 12,073

## Note

# Flame-ionization detectors for the analysis of some inorganic gases

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(First received March 9th, 1979; revised manuscript received May 31st, 1979)

The flame-ionization detector (FID) is probably the most widely used sensitive detector in chromatography and its response to organic compounds has been widely investigated[1–5]. It has also been recognized that under conventional operating conditions the FID has a negligible response to inorganic gases[6–8]. Some workers[9–11] have enhanced its response to inorganic gases by using a continuous supply of methane in the flame. It was recently found that a Pye Unicam Series 104 FID, operated in a hydrogen-rich mode with oxygen to support combustion, can greatly enhance the response to some inorganic gases[12]. The noise level and the detection limit for nitric oxide are given in Tables I and II.

TABLE I

PARAMETERS OF PYE SERIES 104 FID OPTIMIZED FOR NO DETECTION

Data from ref. 12.

| *Parameter* | *Value* |
|---|---|
| Noise level | $1 \cdot 10^{-13}$ A |
| Standing current | $2 \cdot 10^{-10}$ A |
| Response | $1 \cdot 10^{-2}$ C/g |
| Reproducibility of response | 0.6% |
| Linear dynamic range | $10^3$ |

TABLE II

RESPONSE DATA FOR PYE UNICAM SERIES 104 FID

Data from ref. 12.

| *Gas* | *Response (C/g)* | *Detection limit (g/sec)* |
|---|---|---|
| Ar | $3 \cdot 10^{-8}$ | $7 \cdot 10^{-6}$ |
| $CH_4$ | $1 \cdot 10^{-2}$ | $2 \cdot 10^{-11}$ |
| CO | $2 \cdot 10^{-6}$ | $4 \cdot 10^{-7}$ |
| $CO_2$ | $5 \cdot 10^{-6}$ | $4 \cdot 10^{-8}$ |
| He | $4 \cdot 10^{-6}$ | $5 \cdot 10^{-8}$ |
| $H_2S$ | $5 \cdot 10^{-4}$ | $4 \cdot 10^{-10}$ |
| NO | $1 \cdot 10^{-2}$ | $2 \cdot 10^{-11}$ |
| $N_2O$ | $3 \cdot 10^{-5}$ | $7 \cdot 10^{-9}$ |
| $NO_2$ | $1 \cdot 10^{-4}$ | $2 \cdot 10^{-9}$ |
| $O_2$ | $4 \cdot 10^{-6}$ | $5 \cdot 10^{-8}$ |
| $SO_2$ | $5 \cdot 10^{-4}$ | $4 \cdot 10^{-10}$ |

All of the data in Table II (except those for nitric oxide and methane) were obtained at a standing current of $4 \cdot 10^{-10}$ A and only the signal for carbon dioxide is a linear negative one.

This paper describes some experiments carried out with different FIDs in order to determine their applicability to the analysis of inorganic gases. The construction of an FID designed in this Institute is presented.

## EXPERIMENTAL

Different types of chromatographs with their original FIDs were used. Nitrogen oxide, with a concentration of 0.05% in nitrogen, was injected on to a Porapak Q column by means of a sampling valve with a 1-ml capacity loop. The carrier and diluent gases were nitrogen.

## RESULTS AND DISCUSSION

Using the same operating conditions, the FIDs of the following chromatographs were tested for NO: Pye Unicam Series 104, Carlo Erba Model 450, Tswett 100, Perkin-Elmer F7, Termochrom 23 (designed in this Institute and Becker 409. The flow-rates of the gases were as follows: nitrogen, 20; hydrogen, 55; and oxygen, 40 ml/min.

The detection limits for the FIDs are given in Table III.

TABLE III

DETECTION LIMITS FOR NO USING VARIOUS FIDS

| *FID* | *Detection limit (g/sec)* |
|---|---|
| Pye Unicam Series 104 | $2 \cdot 10^{-11}$ |
| Becker 409 | $8 \cdot 10^{-11}$ |
| Carlo Erba Model 450 | $\approx 1 \cdot 10^{-9}$ |
| Tswett 100 | $\approx 1 \cdot 10^{-9}$ |
| Termochrom 23 | $8 \cdot 10^{-10}$ |
| Perkin-Elmer F7 | $\approx 1 \cdot 10^{-9}$ |

It is evident that all of the detector gave signals for NO, but only the first two can operate in a hydrogen-rich mode. An excessive amount of condensed water vapour gave rise to a drastic increase in the noise of the other detectors, and they could be operated in that mode only if the collector electrode and the gas outlet cap were changed.

The sensitivities of the FIDs decrease after continuous operation in a hydrogen-rich mode, owing to oxidation of the collector electrode. The sensitivities can be restored by increasing the hydrogen flow-rate or by mechanical cleaning of the collector electrodes. It is preferable for the collector electrode to be cleaned once a week.

Different constructions of the Termochrom 23 FID were tested and with that shown in Fig. 1, good results were obtained. With the flow-rates specified above, the standing current of this detector is $3.5 \cdot 10^{-10}$ A and the noise level is $1 \cdot 10^{-13}$ A.

Using this chromatograph and by means of a sampling valve, 1-ml samples of

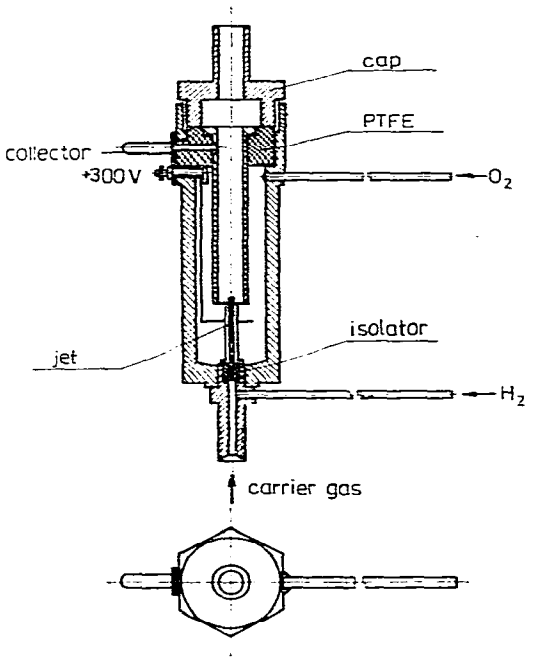


Fig. 1. Cross-section of Termochrom 23 FID.

0.05% NO, 0.07% $NO_2$ 0.06% $SO_2$, and 0.06% $H_2S$ in nitrogen were injected on to a Porapak Q column. The response data are given in Table IV.

The reproducibility (six injections) is 0.5% and the linear dynamic range is $>10^4$ (Fig. 2).

A series of analyses for the determination of the nitrogen oxide content in diesel engine exhaust gases was carried out with the Termochrom 23 FID. The chromatogram in Fig. 3 was obtained from 1-ml sample injected on to a Porapak Q column. The negative $CO_2$ peak can be avoided by using a 10–15-cm pre-column packed with molecular sieve 5A. The results of this work will be published separately.

Direct observation of the flame when different inorganic gases were passed through it was carried out. The hydrogen-rich colour is more intense than that when conventional operating conditions are used and is yellowish. The flame becomes intense white wity a very slight bluish tint when an organic compound passes, and very slightly greeen when an inorganic gas passes. The flame colour hardly changes when argon and helium are passed through. And it loses its colour only when carbon dioxide

TABLE IV

RESPONSES AND DETECTION LIMITS FOR INORGANIC GASES USING TERMOCHROM 23 FID

| *Gas* | *Response (C/g)* | *Detection limit (g/sec)* |
|---|---|---|
| NO | $1 \cdot 10^{-2}$ | $2 \cdot 10^{-11}$ |
| $NO_2$ | $5 \cdot 10^{-4}$ | $4 \cdot 10^{-10}$ |
| $SO_2$ | $2 \cdot 10^{-3}$ | $1 \cdot 10^{-10}$ |
| $H_2S$ | $2 \cdot 10^{-3}$ | $1 \cdot 10^{-10}$ |

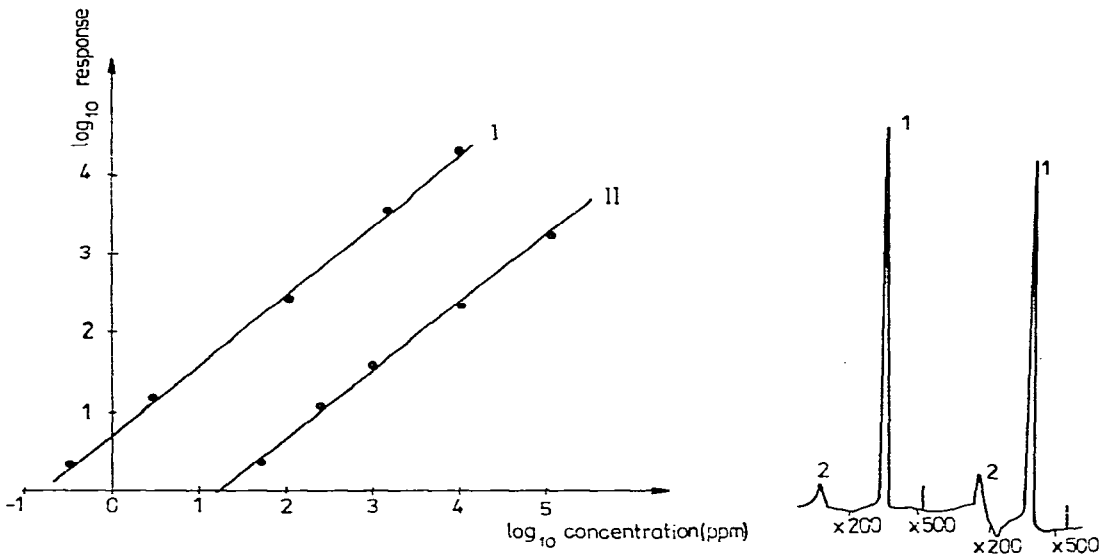


Fig. 2. Linearity of response. I, NO; II, $SO_2$ and $H_2S$.

Fig. 3. Typical gas chromatogram of exhaust gas from diesel engine. Peaks: 1 = NO; 2 = $NO_2$.

passes. The carbon dioxide signal decreases gradually and becomes positive on increasing the standing current by increasing the hydrogen and oxygen flow-rates. A maximal positive carbon dioxide signal is reached at a standing current of $2 \cdot 10^{9}$–$4 \cdot 10^{-9}$ A, but from visual observation the jet and the collector electrode are bright red and there is considerable noise. Under these conditions the use of the FID is not possible. We believe that the FID operating in a hydrogen-rich mode can be used with a standing current not higher than $4.5 \cdot 10^{-10}$ A. The above observations make possible the assumption that argon and helium signals in Table II is due to pollution.

Carbon dioxide gives a negative signal as the result of flame cooling and a decrease in the standing current. Samples of oxygen and hydrogen passing through the flame increase the jet temperature and the emission current gives a positive signal.

As carbon monoxide is combustible it should have the same effect as a small increase of hydrogen, but the results show that the carbon monoxide response depends on the hydrogen to oxygen ratio. The best ratio of nitrogen, hydrogen and oxygen flow-rates for the hydrogen-rich flame mode is 1:3:1.5.

Typical ionization is observed when NO, $NO_2$, $SO_2$, $H_2S$ and CO pass through the flame. Probably chemical ionization rather than thermal ionization is responsible.

Using hydrogen-rich flames, different investigations of the analysis of heteroorganic compounds have been reported[13,14]. Response data for many organometallic and phosphorus-, sulphur- and halogen-containing compounds have been given for very high hydrogen flow-rates (830–1600 ml/min), but it is clear that such flow-rates are possible only with specially constructed detectors based on the flame photometric detector and the alkali-FID.

Some preliminary investigations have shown that the Termochrom FID operating in a hydrogen-rich mode has a higher response than the conventional FID for many organophosphorus, -sulphur and -chlorine coumpounds. Investigations of the response to organophosphorus and -sulphur compounds are continuing.

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