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## A DUAL-MODE INDIUM FLAME DETECTOR\*

ROBERT F. MOSEMAN\*\* AND WALTER A. AUE\*\*\*

*Department of Agricultural Chemistry, University of Missouri, Columbia, Mo. 65201 (U.S.A.)*

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## SUMMARY

A normal flame ionization detector has been modified such that the flame burns in contact with liquid indium and the emission from indium or its halides can be detected by a spectrometer or a filter-photomultiplier combination. The flame ionization detector's response is unimpaired by the presence of indium and may be monitored simultaneously with the photometric signal. By choice of spectrometer wavelength it is possible to ascertain whether a compound eluted from the gas chromatograph contains chlorine, bromine, or iodine.

## INTRODUCTION

To an increasing extent, gas chromatographic (GC) analysis relies upon a variety of highly selective detectors. Several of these utilize optical emission obtained from a hydrogen flame in which the compounds emerging from the chromatographic column are combusted. The most notable example is probably the phosphorus-sulfur detector first described by BRODY AND CHANEY<sup>1</sup>.

Photometric detectors in general have been adequately reviewed<sup>2-5</sup>. This paper deals with a somewhat unique detection principle and its application in a normal flame ionization detector (FID). In 1966, GILBERT used indium and a dual flame burner in an effort to determine chlorine, similar to the well-known Beilstein reaction of halides with copper. He found, however, that the molecular emission of InCl was more pronounced and selective for chlorine than the atomic In lines<sup>6</sup>.

GUTSCHE AND HERRMANN further developed the indium flame detector and used it in series with a thermal conductivity cell on GC effluents. The InCl band at 3600 Å signaled chlorine, the InBr band at 3727 Å indicated bromine<sup>7,8</sup>. BOWMAN *et al.*<sup>9</sup> described a single-flame indium detector similar to their version of the Beilstein detector<sup>10</sup> and obtained excellent selectivity for Cl, Br, or I vs. carbon compounds at the 3600 Å wavelength.

Further research in this field, although not directly connected with GC, can be found in the papers by DAGNELL *et al.*<sup>11</sup> and OVERFIELD AND WINEFORDNER<sup>12</sup>.

The use of hydrogen as a fuel is common to all described indium flames (as we shall call them for the sake of brevity), but there the similarity ends. Under-

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\*\* Material taken from doctoral thesis.

\*\*\* To whom reprint requests should be directed.

standably, the variety of flame conditions, indium configurations, and optical hardware has resulted in some disparity in performance characteristics. GILBERT<sup>6</sup> as well as GUTSCHE AND HERRMANN<sup>7</sup>, for instance, indicate that chlorine can be determined specifically from the InCl bands, while BOWMAN *et al.*<sup>9</sup> find that chlorine, bromine, and iodine compounds respond equally well at the 3600 Å wavelength.

Although the indium flames vary widely in configuration and composition, none is quite comparable to the puny hydrogen flame used in the familiar FID. Optimal halide response seems to require much larger flames.

Our own interest in the matter was not to devise yet another indium flame, but to dope a run-of-the-mill FID with indium and observe the spectral as well as the electrical effects. This dual-mode detector was deliberately run at flow rates typical of the FID. It was our goal to define the optical characteristics of this simple device and utilize it to distinguish from each other, compounds containing chlorine, bromine, iodine, or no halogen at all.

#### EXPERIMENTAL

The detector arrangement is shown in Figs. 1 and 2 and is largely self-explanatory. It is similar to one we used earlier for measuring an alkali flame detector's spectral response<sup>13</sup>, except that the housing was now made of cast aluminum (cour-

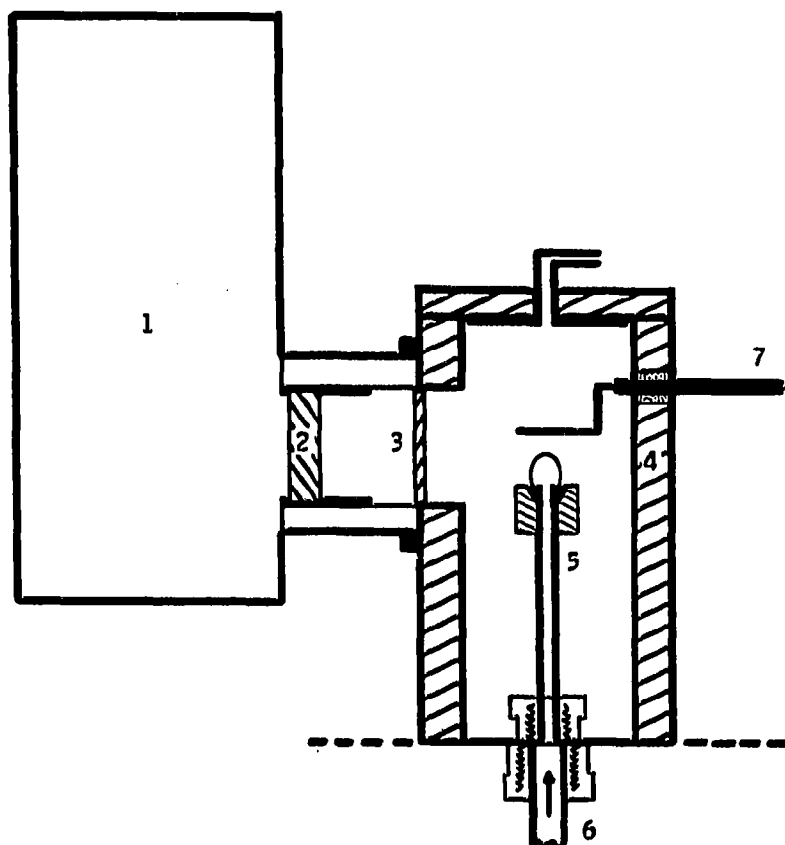


Fig. 1. Dual-mode indium flame detector (DMIFD). (1) Photomultiplier tube assembly; (2) interference filter; (3) quartz window; (4) aluminum detector housing; (5) detector jet tip assembly; (6) GC column; (7) collector electrode assembly.

tesy R. J. Moseman, Federal Pattern Works and Foundry, Indianapolis, Ind. U.S.A.), and a platinum electrode enters the housing through appropriate Teflon insulation. This arrangement is akin to several commercially available FID's.

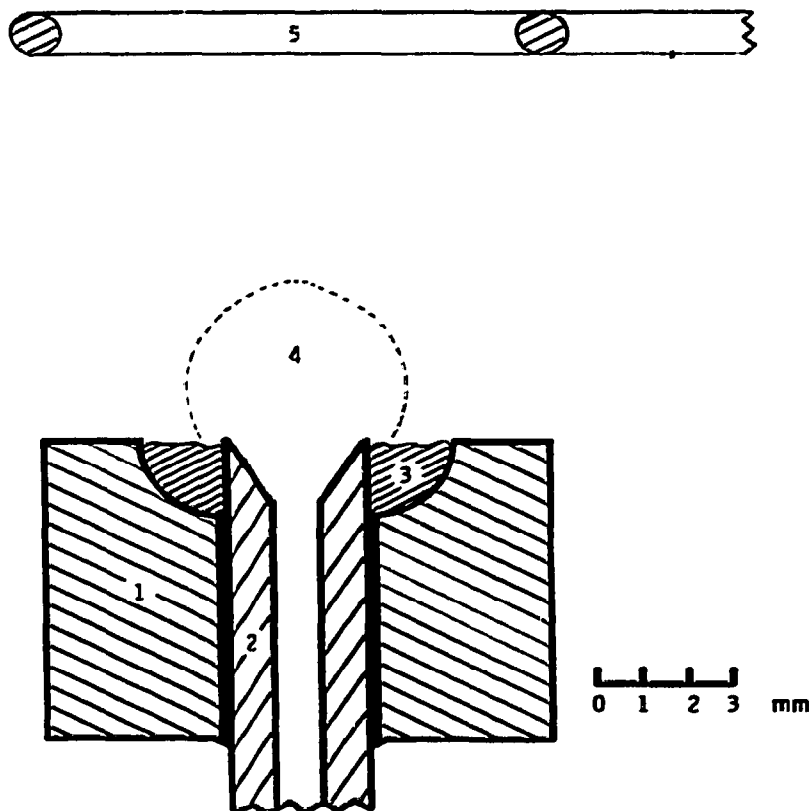


Fig. 2. Dual-mode indium flame detector (detail). (1) Steel cup; (2) detector jet tip; (3) indium metal; (4) hydrogen flame; (5) collector electrode.

Fig. 1 shows the detector in conjunction with interference filter and photomultiplier, directly on top of the chromatographic column. Not visible is a stream of laboratory air directed at the photomultiplier housing and adaptor to keep it cool. Two interference filters were purchased in a sale, one 1/2 in. square (3609 Å, 20 Å width at half height, 20% transmission), nominally for InCl emission; and one 1 in. disc (4111 Å, 105 Å, and 60% respectively) for the In atomic line. It should be understood in this context that the choice of filters was based partially on monetary considerations and does not represent the optimal optical solution.

When the detector was to be used with the spectrometer, the photomultiplier-filter part was removed and the detector housing with the quartz window held directly against the spectrometer's entrance slit. In this case, column effluents were transferred from the gas chromatograph via heated stainless steel tubing. Hydrogen and air inlets, which are not shown in Fig. 1, were similar to commercial constructions.

The FID channel consisted of a Barber-Colman battery box (—240 V on the electrode), connected to a matched-tube electrometer from the same company. The photometric channel used an RCA 931-A photomultiplier tube with a Keithley 240-A power supply and 417 picoammeter. Either the arrangement shown in Fig. 1, or a Jarrel-Ash 82-000 half meter Ebert scanning spectrometer provided spectral

resolution. Due to the lack of a dual-channel device, two single-channel potentiometric strip-chart recorders were used.

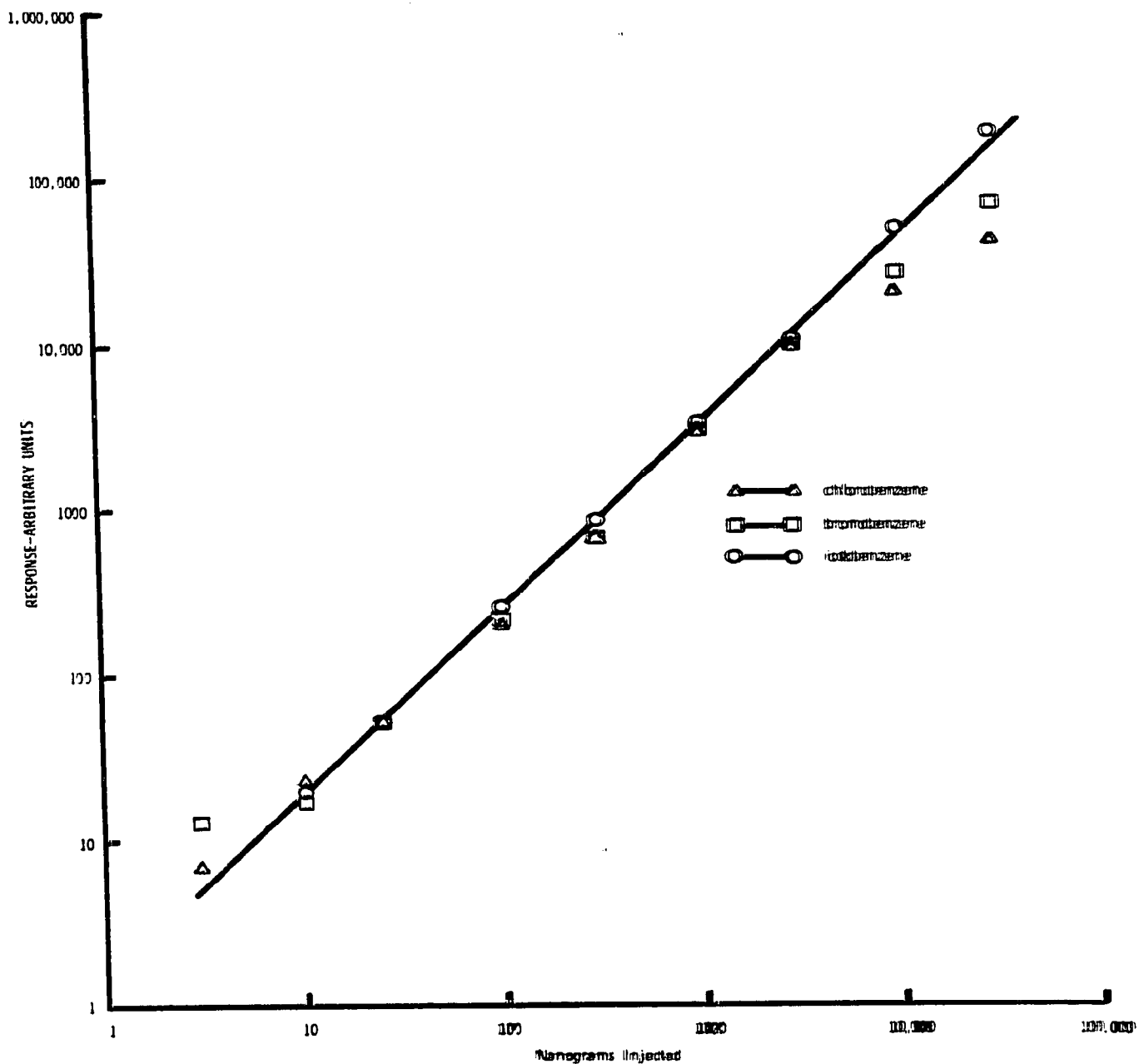


Fig. 3. Halogenated benzene response. Column: 5% Carbowax 20 M on 80-100 mesh Chromosorb W-HP, 1.3 m  $\times$  4 mm I.D. Pyrex; oven temperature: 110 $^{\circ}$ ; flow rates in ml/min: N<sub>2</sub> = 25, H<sub>2</sub> = 60, air = 240; DMIFD, 4111 Å filter.

The gas chromatograph was a modified RAC-1500 column conditioning oven. Columns and test substances were selected in regard to analytical expedience and bore no further significance. All other details are given in the figure legends.

## RESULTS AND DISCUSSION

In initial studies, the nitrogen carrier gas was doped with chlorobenzene, bromobenzene, and iodobenzene, as well as with fluorobenzene and benzene, contained in a U-tube. The spectrometer scans corresponded well to those reported in the literature<sup>10,11</sup>. No spectrum was observed for fluorobenzene or benzene in the 3000–4600 Å region.

Calibration curves were run for the three responsive halobenzenes using the two interference filters as well as the spectrometer set at various significant wavelengths. By far the most notable example is shown in Fig. 3, obtained by monitoring the atomic In line at 4098 Å (uncorrected value) with an interference filter. The InI band at 4094 Å adds to the response for iodobenzene but the contribution is small.

The filters are obviously much more sensitive and much less selective than the spectrometer. The deviation from the linear range on a log-log plot occurs at about the same compound concentration on either readout. Chlorobenzene tails off first, presumably because more chlorine than bromine or iodine atoms are introduced into the flame by equal-weight injections. Since the filters, however, allow the log-log plot to be extended into the lower nanogram regions, the apparent linear range is larger. Characteristically, analysis by spectrometer is limited by phototube noise, analysis by filter-photomultiplier is limited by flame noise.

Very little selectivity could be obtained for chlorine with the filter at 3600 Å in regard to the other halogens. In this case, our results are similar to those reported by BOWMAN *et al.*<sup>9</sup>. These authors, however, were able to obtain far better halogen-carbon selectivity ratios than our small flame was able to provide. Relative halide responses varied somewhat with flow conditions, but their analytical applicability is questionable.

Nitrogen compounds showed no effect; but sulfur or phosphorus containing compounds gave enhanced responses when compared to hydrocarbons. Phosphates, unfortunately, also appeared to diminish the response of subsequently injected halides.

Keeping indium in a reservoir at the base of the flame worked well and provided good performance for several weeks. We have not tested the lifetime of this simple arrangement (Fig. 2) under heavy analytical use, but would expect it to compare favorably with the indium sources reported in the literature.

The flame ionization response was not significantly altered by the presence of indium as could be easily shown by using a plain jet tip. No particular effort was made, however, to define possible minor effects of indium on the signals originating from different types of compounds.

A comparison of the two modes of detection as well as a visual demonstration of the selectivity obtainable from the spectrometer, is shown in Fig. 4. The same mixture, containing 1 µg of each halobenzene per µl of hexane, was injected repeatedly, varying only the spectrometer wavelength setting.

Several conclusions can be drawn from these and similar experiments. Selectivity ratios for halides *vs.* carbon compounds are generally between three to four orders of magnitude. They can be improved, at a cost in sensitivity, by using narrower spectrometer slits, especially for the atomic In lines. Among these, the 4507 Å line is preferable to the one at 4098 Å (all wavelengths uncorrected).

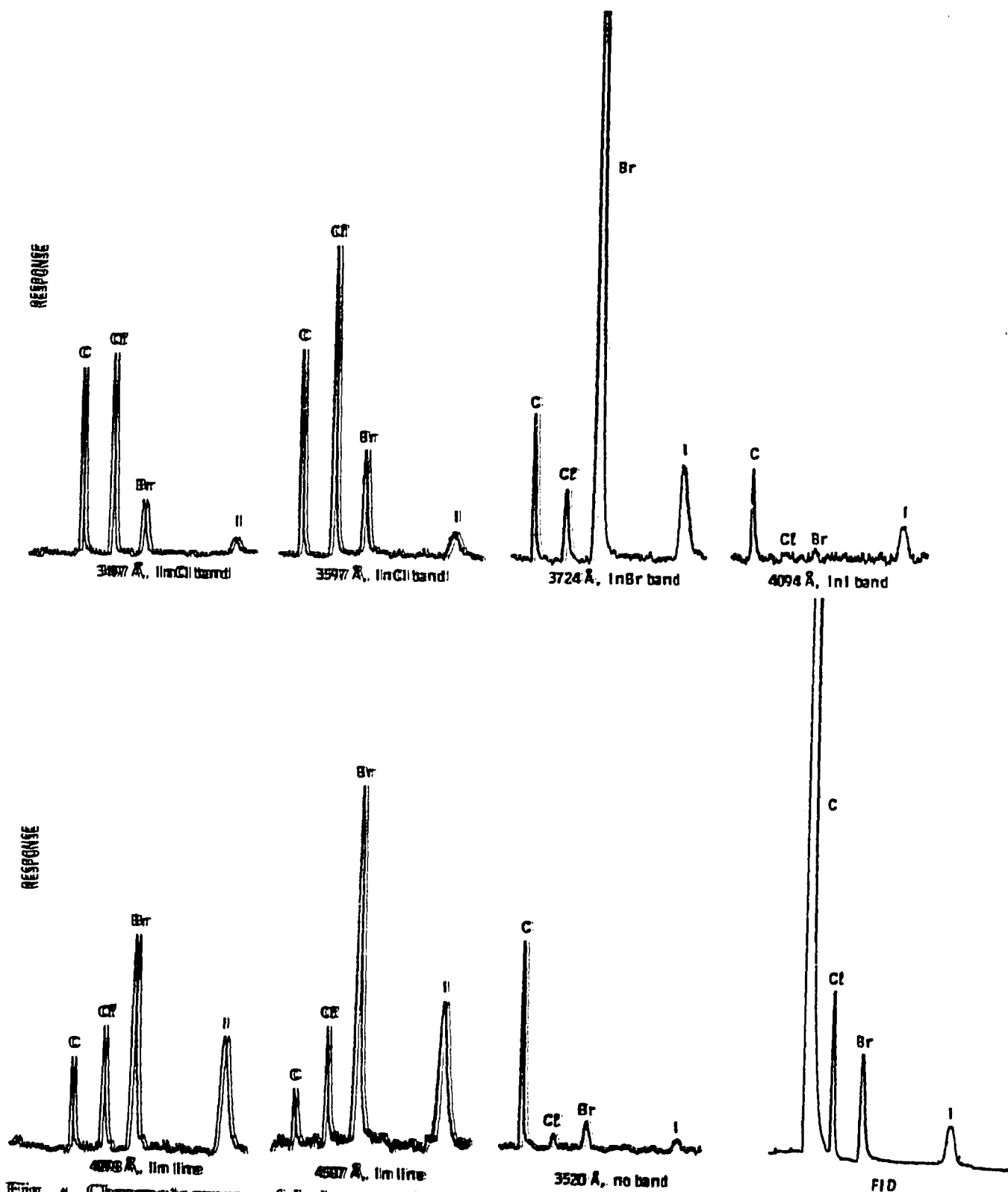


Fig. 4. Chromatograms of halogenated benzenes. C = 1  $\mu$ l hexane; Cl = 1  $\mu$ g chlorobenzene; Br = 1  $\mu$ g bromobenzene; I = 1  $\mu$ g iodobenzene; column: 5% Carbowax 20M on 80-100 mesh Chromosorb W-HIP, 1.3 mm  $\times$  4mm I.D. Pyrex; oven temperature: 110 $^{\circ}$ ; flow rates in ml/min:  $N_2$  = 25,  $H_2$  = 50, air = 240; Jarrel-Ash 82-000, 250  $\mu$  slits; photometric  $1 \cdot 10^{-9}$  A.F.S., ioniza-

We did not experience the difficulties in resolving the InI band from the In line in the 4100 Å region as had been reported by other authors using different optical hardware. (Our spectrometer is capable of 0.2-Å resolution with 10- $\mu$  slits.) The 4094 Å band can thus be used for selective iodine analysis. Selectivities, however, are small among the halides themselves. Yet, it is no problem to determine from the chromatograms whether a compound contains chlorine, bromine, iodine, or none of these. This was proven out by giving three "unknown" solutions to a cooperative graduate student who was able, within less than an hour, to indicate correctly the nature of the halogen in each of the six compounds listed in Table I. Hydrocarbons, of course, would have been immediately apparent by checking the simultaneous FID response. One can get a very rough idea of how much halogen is contained in a particular molecule by comparing the electrical with the optical channel, but the present reliability of such conclusions is, to say the least, very low.

TABLE I

UNKNOWN SOLUTIONS USED FOR HETERO-ATOM DETERMINATIONS

<i>Solution number</i>	<i>Concentration of compound 1</i>	<i>Concentration of compound 2</i>
1	0.5 $\mu\text{g}/\mu\text{l}$ <i>p</i> -dichlorotoluene	0.5 $\mu\text{g}/\mu\text{l}$ <i>sym.</i> -tetrachloroethane
2	1 $\mu\text{g}/\mu\text{l}$ <i>p</i> -dichlorotoluene	0.6 $\mu\text{g}/\mu\text{l}$ bromobenzene
3	1 $\mu\text{g}/\mu\text{l}$ <i>sym.</i> -tetrachloroethane	2 $\mu\text{g}/\mu\text{l}$ iodobenzene

Our flame, which is typical of the ionization detector, gave somewhat better photometric response for the atomic indium emission than for the indium halide bands, but the preference was not very pronounced. The best overall response was obtained from bromine compounds. In this context, the paper by GUTSCHE AND HERMANN should be mentioned, since they first described the indium flame as a selective detector for organobromine compounds<sup>8</sup>.

We regarded the good photometric performance of what is essentially a FID as a pleasant surprise. Furthermore, the simple construction and apparent stability of the indium source made the detector easy to install and handle. Its potential for characterizing unknown compounds in the dual-mode as well as determining the nature of possible halogens involved, were considered added advantages.

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## REFERENCES

- 1 S. S. BRODY, AND J. E. CHANEY, *J. Gas Chromatogr.*, 4 (1966) 42.
- 2 A. V. NOVAK, AND H. V. MALMSTADT, *Anal. Chem.*, 40 (1968) 1108.
- 3 F. A. GUNTHER, A. LOPEZ-ROMAN, R. I. ASAI AND W. E., WESTLAKE, *Bull. Environ. Contam. and Toxicol.*, 4 (1969) 202.

- 4 M. KREJČI AND M. DRESSLER, *Chromatogr. Rev.*, 13 (1970) 1.
- 5 H. C. HARTMANN, *Anal. Chem.*, 43 (1971) 113A.
- 6 P. T. GILBERT, *Anal. Chem.*, 38 (1966) 1920.
- 7 B. GUTSCHE AND R. HERRMANN, *Z. Anal. Chem.*, 245 (1969) 274.
- 8 B. GUTSCHE AND R. HERRMANN, *Z. Anal. Chem.*, 249 (1970) 168.
- 9 M. C. BOWMAN, M. BEROZA AND G. NICKLESS, *J. Chromatogr. Sci.*, 9 (1970) 44.
- 10 M. C. BOWMAN AND M. BEROZA, *J. Chromatogr. Sci.*, 7 (1969) 484.
- 11 R. N. DAGNELL, D. J. SMITH, K. C. THOMPSON AND T. S. WEST, *Analyst*, 94 (1969) 643.
- 12 C. V. OVERFIELD AND J. D. WINEFORDNER, *J. Chromatogr. Sci.*, 8 (1970) 233.
- 13 W. A. AUE AND R. F. MOSEMAN, *J. Chromatogr.*, 61 (1971) 35.

*J. Chromatogr.*, 63 (1971) 229-236