

CHROM. 4227

## RESPONSE OF THE ALKALI FLAME IONIZATION DETECTOR TO HALOGEN COMPOUNDS

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(Received June 18th, 1969)

## SUMMARY

The response of the alkali flame ionization detector to halogen compounds, as well as the effect of the halogen compound structure on the molar response, have been determined using various alkali metals. An increase in response, as compared with the flame ionization detector, occurs with sodium with chloro and bromo compounds and with sodium and potassium in the case of iodo compounds. The molar responses of various monobromo compounds are approximately equal. The response to the chlorobenzenes increases proportionately to the number of chlorine atoms in the molecule.

## INTRODUCTION

The alkali flame ionization detector (AFID) is a detector which is selective for compounds containing phosphorus<sup>1,2</sup>, halogens<sup>1,2</sup>, nitrogen<sup>3,4</sup>, arsenic<sup>4,5</sup>, and sulphur<sup>6</sup>. The sensitivity of detection is dependent on a number of working parameters, *e.g.* the flow rate of the gases<sup>1</sup>, the species of alkali cation<sup>7,8</sup>, and the detector geometry<sup>3</sup>. With respect to the time stability of the detector response, the most important parameter is the way the alkali metal salt is placed in the flame; the most convenient method seems to be the use of a jet tip made of compressed salt<sup>9</sup>. The performance of the above type of AFID has already been described for compounds containing phosphorus<sup>9-12</sup>, nitrogen<sup>11-13</sup>, and sulphur<sup>6</sup>.

The selectivity of the AFID to halogen compounds was described as early as in the first papers on this detector<sup>1,2</sup>. However, it would seem from the literature that the AFID response to this type of compound depends essentially on the detector design. For instance, it has been found by JANÁK AND SVOJANOVSKÝ<sup>14</sup> that the detector is sensitive, selectively, to halogen containing compounds when using all alkali metals; similarly, KARMEN<sup>15</sup> has found that the relative sensitivity towards compounds with phosphorus and chlorine varies only a very little with the use of various alkali metals. On the other hand, GIUFFRIDA *et al.*<sup>7</sup> found that the response

to halogen compounds may be suppressed by the use of KCl or KBr; HARTMANN<sup>9</sup> has even found that the response to chloro compounds may be, under certain conditions, negative. The aim of the present work was to follow in greater detail the response of an AFID, with a compacted alkali metal salt jet tip, to halogen compounds.

#### EXPERIMENTAL

The AFID used had a jet tip of a compressed alkali metal salt and its design has been described by us earlier<sup>6</sup>. This detector was built-in into a CHROM 3 Gas Chromatograph (Laboratory Equipment, N.E., Prague). A 68 cm long stainless steel column of 0.6 cm open diameter, packed with 5 wt % of polyethylene glycol-on-Sterchamol (80-100 mesh) was used for the chromatography of the model halogen compounds. The column temperature was 90°. The compounds chromatographed were dissolved in hexane and injected with a Hamilton microsyringe.

The flow rates of the carrier gas and air were 60 and 660 ml/min, respectively, the hydrogen flow rate was varied so as to obtain the required background current value.

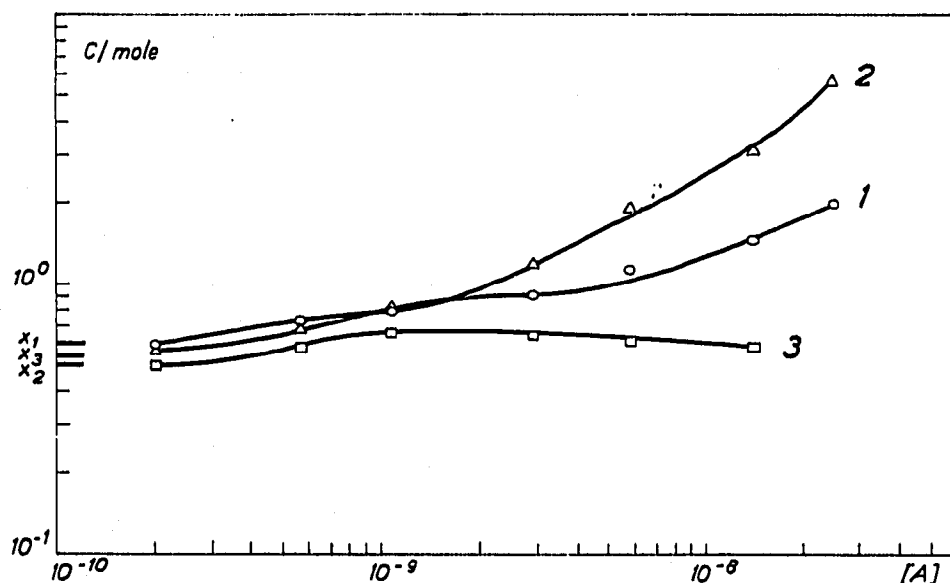


Fig. 1. Dependence of the response on the background current using a sodium salt. 1 = Chlorobenzene; 2 = bromobenzene; 3 = iodobenzene.  $x_1$ ,  $x_2$ , and  $x_3$  = FID ionization efficiencies for chlorobenzene, bromobenzene, and iodobenzene, respectively, at optimum  $H_2$  and  $N_2$  flow rates.

#### RESULTS

Figs. 1-3 show the dependence of the molar responses of chloro-, bromo-, and iodobenzene on the background current when using Na, K, and Cs salts. In case of the sodium salt (Fig. 1) an enhancement in response, as compared to the FID, comes about with all three compounds, and the response to chloro- and bromobenzene rises in dependence on the background current, while the response to iodobenzene displays a maximum in the region  $1-2 \times 10^{-9}$  A. The response increases in the sequence:  $I < Cl < Br$  compound.

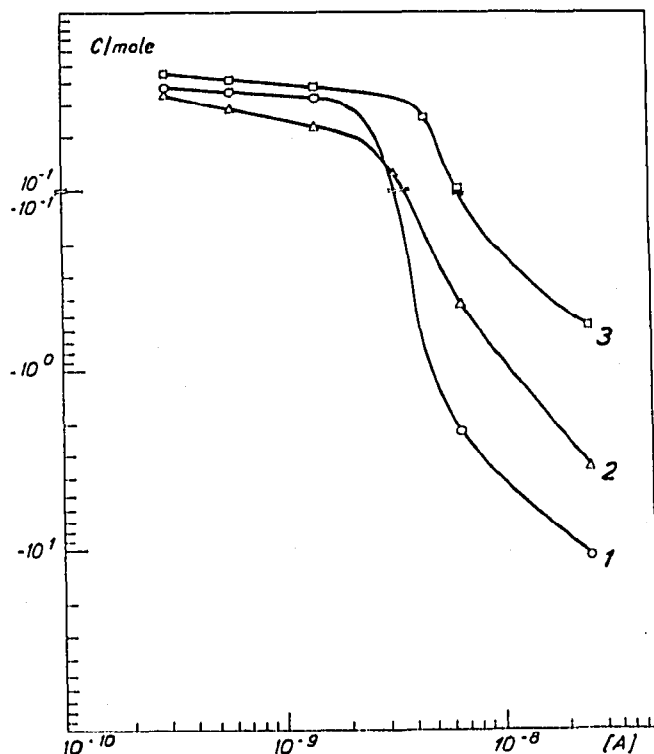
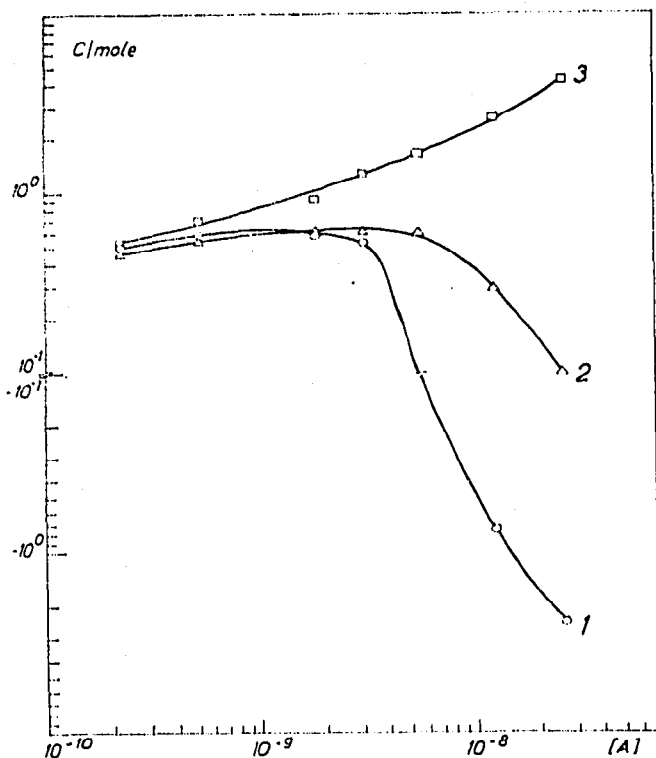


Fig. 2. Dependence of the response on the background current using a potassium salt. 1 = Chlorobenzene; 2 = bromobenzene; 3 = iodobenzene.

Fig. 3. Dependence of the response on the background current using a caesium salt. 1 = Chlorobenzene; 2 = bromobenzene; 3 = iodobenzene.

Unlike the sodium salt, where an increase in the ionization current occurs with all the halogen benzenes on passing them through the detector, the use of the potassium salt (Fig. 2) leads to an increase in the ionization current over the whole region of background currents investigated only with iodobenzene. With chloro- and bromobenzene a decrease in the ionization current occurs at a certain background current value, the latter being lower for chlorobenzene than for bromobenzene; the response is negative under these conditions.

With caesium salt a decrease in the ionization current occurs with all three halogen benzenes, and the background current incidental to a negative response increases in the order: Cl < Br < I.

It is apparent from Figs. 1-3 that the courses of the background current dependence of the response to the individual halogen benzenes are considerably different. In order to prove whether this course is invariable for a given halogen, the above relationships were followed for various bromo compounds (bromocyclohexane, bromotoluene, and bromocymene) employing sodium and potassium salts. These relationships, relative to that of bromocyclohexane which was used as a reference compound, are illustrated in Figs. 4 and 5. In both cases, *i.e.* both with Na and K the response to the individual bromo compounds is different within the region of lower background currents. When employing potassium salts the courses are different up to approx.  $1.5 \times 10^{-8}$  A, when the response to all the three bromo compounds

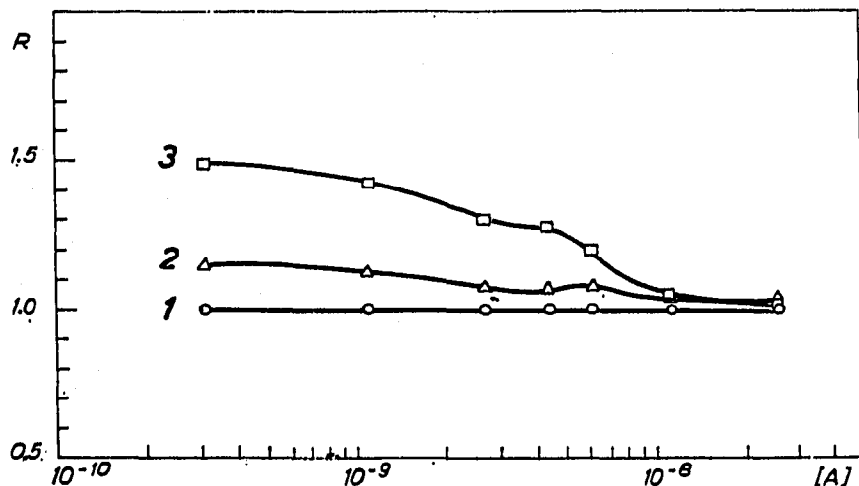


Fig. 4. Dependence of the response on the background current using a sodium salt. 1 = Bromocyclohexane; 2 = bromotoluene; 3 = bromocymene; R = relative response.

becomes negative. At higher background currents, when a decrease in the ionization current occurs, the responses are approximately the same. When a sodium salt is used the courses of the response to the above compounds are different up to about  $1 \times 10^{-8}$  A.

The effect of structure on the response was investigated on a number of mono-bromo derivatives of benzene, toluene, cyclohexane, cymene, and styrene, at a background current of  $1 \times 10^{-8}$  A (Table I), using a sodium salt. The ionization efficiencies of the above bromo compounds, expressed in Coulombs/mole compound, are, under the given conditions, approximately equal.

Table I also summarizes the ionization efficiencies of mono-, di-, tri-, and tetrachlorobenzene. As a single burner AFID is also sensitive to carbon compounds the response to chlorobenzene is not solely due to the presence of the chlorine atom.

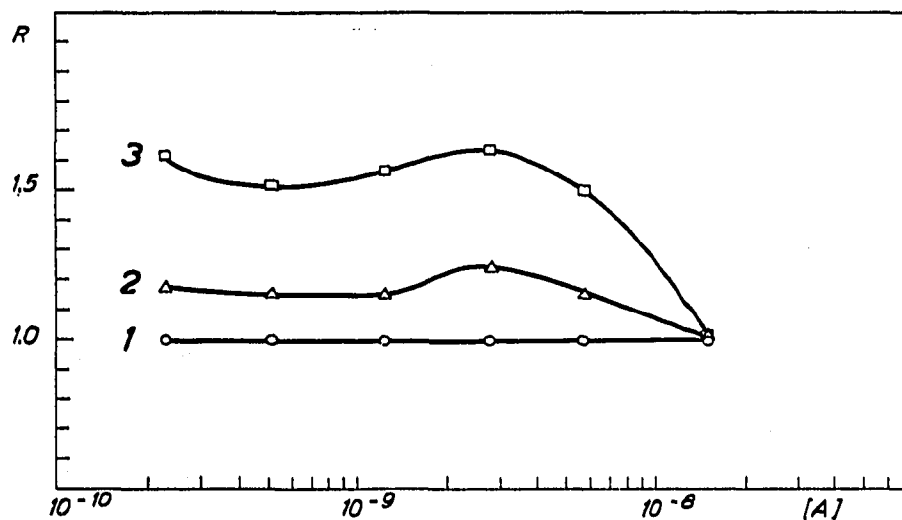


Fig. 5. Dependence of the response on the background current using a potassium salt. 1 = Bromocyclohexane; 2 = bromotoluene; 3 = bromocymene; R = relative response.

TABLE I

MOLAR RESPONSE OF SOME HALOGEN COMPOUNDS

Compound	Ionization efficiency	
	in Coulombs/ mole	in Coulombs/ gram atom Cl
Chlorobenzene	1.38	1.38
1,4-Dichlorobenzene	2.79	1.40
1,3,5-Trichlorobenzene	4.10	1.37
1,2,4,5-Tetrachlorobenzene	5.53	1.38
Bromocyclohexane	2.4	
4-Bromotoluene	2.5	
$\beta$ -Bromostyrene	2.2	
Bromobenzene	2.4	
2-Bromocymene	2.5	

The contribution of the carbon skeleton (benzene) was therefore subtracted from the ionization efficiency found for the molecule of the benzene chloro derivatives. It can be seen from Table I that the ionization efficiency so obtained increases in relation to the number of chlorine atoms in the molecule of the substance under investigation, the contribution of the individual chlorine atoms being equal.

## DISCUSSION

It seems from the dependence of molar response of bromo compounds on the background current that the differences in the detector responses occur within a region where the ionization efficiency of the AFID is not very different from that of the FID for the given flow rates of the gases. In the background current region, where the responses to compounds, with a given heteroatom, are considerably different (either with respect to the magnitude or direction) the molar responses are approximately equal. In the case of the bromo compounds and sodium salt the limiting current is about  $1 \times 10^{-8}$  A above this value the response begins to increase sharply. With potassium salts, it is about  $1.5 \times 10^{-8}$  A when the response becomes negative. A similar course is shown by sulphur compounds, where the differences in response are exhibited up to values of  $4 \times 10^{-10}$  A, when the response becomes, in the case of potassium salts, negative.

It can be inferred from the data obtained that, with this type of detector, the mechanism of response appurtenant to the AFID is overlapped by the mechanism characteristic of the FID. This effect is especially remarkable at lower background currents (lower alkali metal concentration in the flame and lower ionization of the metal) when the molar response increases with the number of carbon atoms in the molecule. At higher background currents (higher alkali metal concentration and higher degree of ionization) there is an apparent preponderance of the AFID mechanism, and, therefore, the molar responses for a given element are approximately equal.

The response of an AFID of the above type to chloro and bromo compounds can be regarded as selective in view of the enhanced response, as compared to the FID, only in the case of sodium salts, while in the case of iodo compounds it is so merely for potassium salt. In other cases the response is dependent on the cation in the sense that the background current at which a negative response occurs varies according to the atomic number of the cation used. In the case of Rb salt the response curve is similar to that with potassium.

Recently, LAKOTA AND AUE<sup>16</sup> reported results for halogen compounds with this type of AFID which were, in certain respects, similar to the phenomena quoted in the present paper. Using rubidium salts, they always obtained a negative response for chloro compounds, while the response to compounds containing Br, I, N, and P was positive.

It is very interesting to compare our results with the findings of HAYHURST AND SUGDEN<sup>17</sup> who followed the changes in the concentration of electrons in the flame in the presence of alkali metals and halogens. They found that in the case of sodium there is an increase in the concentration of electrons in the flame with all halogens (except fluorine), according to the order:  $I < Cl < Br$ ; in the case of potassium this is so only with iodine, and in the case of caesium there is no increase in the concentration of electrons with any halogen. These findings bear a striking qualitative resemblance to the results quoted in the present work.

## REFERENCES

- 1 L. GIUFFRIDA, *J. Assoc. Offic. Agr. Chemists*, 47 (1964) 293.
- 2 A. KARMEN, *Anal. Chem.*, 36 (1964) 1416.
- 3 W. A. AUE, CH. W. GEHRKE, C. R. TINDLE, D. L. STALLING AND CH. D. RUYK, *J. Gas Chromatog.*, 5 (1967) 381.
- 4 N. F. IVES AND L. GIUFFRIDA, *J. Assoc. Offic. Anal. Chemists*, 50 (1967) 1.
- 5 J. JANÁK, V. SVOJANOVSKÝ AND M. DRESSLER, *Collection Czech. Chem. Commun.*, 33 (1968) 740.
- 6 M. DRESSLER AND J. JANÁK, *J. Chromatog. Sci.*, 7 (1969) 451.
- 7 L. GIUFFRIDA, N. F. IVES AND D. C. BOSTWICK, *J. Assoc. Offic. Agr. Chemists*, 49 (1966) 8.
- 8 M. DRESSLER AND J. JANÁK, *Collection Czech. Chem. Commun.*, 33 (1968) 3970.
- 9 C. H. HARTMANN, *Bull. Environ. Contam. Toxicol.*, 1 (1966) 159.
- 10 W. A. AUE AND G. ERTINGSHAUSEN, *154th Am. Chem. Soc. Meeting, Chicago*, Sept. 1967.
- 11 M. DRESSLER AND J. JANÁK, *Collection Czech. Chem. Commun.*, 33 (1968) 3960.
- 12 W. EBING, *Chromatographia*, 1 (1968) 382.
- 13 C. H. HARTMANN, *J. Chromatog. Sci.*, 7 (1969) 163.
- 14 J. JANÁK AND V. SVOJANOVSKÝ, in A. B. LITTLEWOOD, (Editor), *Gas Chromatography 1966*, Inst. Petroleum, London, 1967, p. 166.
- 15 A. KARMEN, *J. Gas Chromatog.*, 3 (1965) 336.
- 16 S. LAKOTA AND W. A. AUE, *157th Am. Chem. Soc. Meeting, Minneapolis*, April 1969.
- 17 A. N. HAYHURST AND T. M. SUGDEN, *Trans. Faraday Soc.*, 63 (1967) 1375.