

CHROM. 5380

## Response of the alkali flame ionisation detector to silicon, tin and lead compounds

The alkali flame ionisation detector (AFID) gives a selective response to compounds, the molecule of which contains certain elements. The response of the AFID is known to be selective for nitrogen<sup>1,2</sup>, phosphorus<sup>3,4</sup>, and arsenic<sup>2,5</sup>. A selective response has further been found to halogens<sup>3,4</sup>, and to sulphur<sup>6</sup>. The selectivity of the AFID response to individual elements differs considerably and depends on the construction of the detector, the alkali metal salt used and the value of the background current (hydrogen flow rate), with the exception of phosphorus in which case the response is always greater than that of the flame ionisation detector (FID)<sup>7-10</sup>. The polarity of the response to halogen and sulphur compounds can be both positive and negative, depending on the above mentioned parameters.

The response of the AFID to group IV elements has not been investigated up to the present time. The response of a single-flame detector to hydrocarbons is known to be lower than that of the FID, while in the case of a double-flame detector no response is obtained at low concentrations of hydrocarbons. A negative response to tin compounds, reproducible only with difficulty, has also been mentioned for the double-flame AFID<sup>5</sup>. An anomalous response to silicon compounds has also been found with the FID<sup>11,12</sup>.

The response of the AFID to group IV compounds, silicon, tin and lead, is studied in detail in this paper.

### *Experimental*

An alkali ionisation detector with a jet tip of a pressed alkali metal salt, the construction of which has been described by the authors earlier<sup>6</sup>, was employed. This detector was built into a Chrom 3 gas chromatograph (Laboratory Equipment, N.E., Prague). A stainless steel column, 68 cm length and 0.6 cm I.D., filled with 20% polyethylene glycol 1500 coated on Chromosorb W (80-100 mesh) was used for the chromatographic analyses of model compounds. Triethoxymethylsilane, tetraethyltin and tetraethyllead were used as model compounds. The chromatographed compounds were dissolved in hexane and sample of about  $5 \times 10^{-7}$  g were dispensed with a Hamilton microsyringe. The column temperature was 55° in the case of the silicon and tin compounds, 85° in that of the lead compound. The carrier gas flow rate was 60 ml of N<sub>2</sub>/min, air flow rate 660 ml/min, hydrogen flow rate was varied in such a way that the required value of the background current was attained.

### *Results and discussion*

The dependence of the AFID response (expressed as relative to the FID response) on the background current for the model compounds of tin, lead and silicon with the use of sodium sulphate is demonstrated in Fig. 1. The response of the AFID to silicon compounds, up to  $1 \times 10^{-9}$  A background current, is lower than that of the FID; above this value of background current it is higher. The response increases with the increasing background current over the whole range of the background current under study. The lower response below  $1 \times 10^{-9}$  A is due to the fact that in this range

of background current the detector operates as an FID and since hydrogen flow rate is not optimal, the detector response is not optimal either. This phenomenon of variations and/or additions of the processes in the detector has been described earlier<sup>8</sup>.

The response of the detector to the lead compound is positive up to approximately  $1 \times 10^{-9}$  A but it is always lower than that of the FID. The reason for the lower response is the same as with the silicon compounds. The response is negative above  $1 \times 10^{-9}$  A. The negative response increases rapidly with increasing background current.

The response of the AFID to tin compounds, over the whole range of the background current, is negative and increases with increasing background current.

The dependence of the response on the background current for a potassium salt is demonstrated in Fig. 2. The response to the silicon compound over the whole range, except for  $1.2 \times 10^{-10}$  A, of the studied background current is higher than that of the FID. The response again increases with the increasing value of the background current.

The response to the lead compound is, with the exception of  $1 \times 10^{-10}$  A, negative over the whole range of the background current examined and its value, similar to that of the tin compound whose response is always negative, again increases with the increasing background current.

In the case of rubidium and cesium salts the dependence of the response to the model compounds on the background current is similar; only the response increases and is highest for cesium.

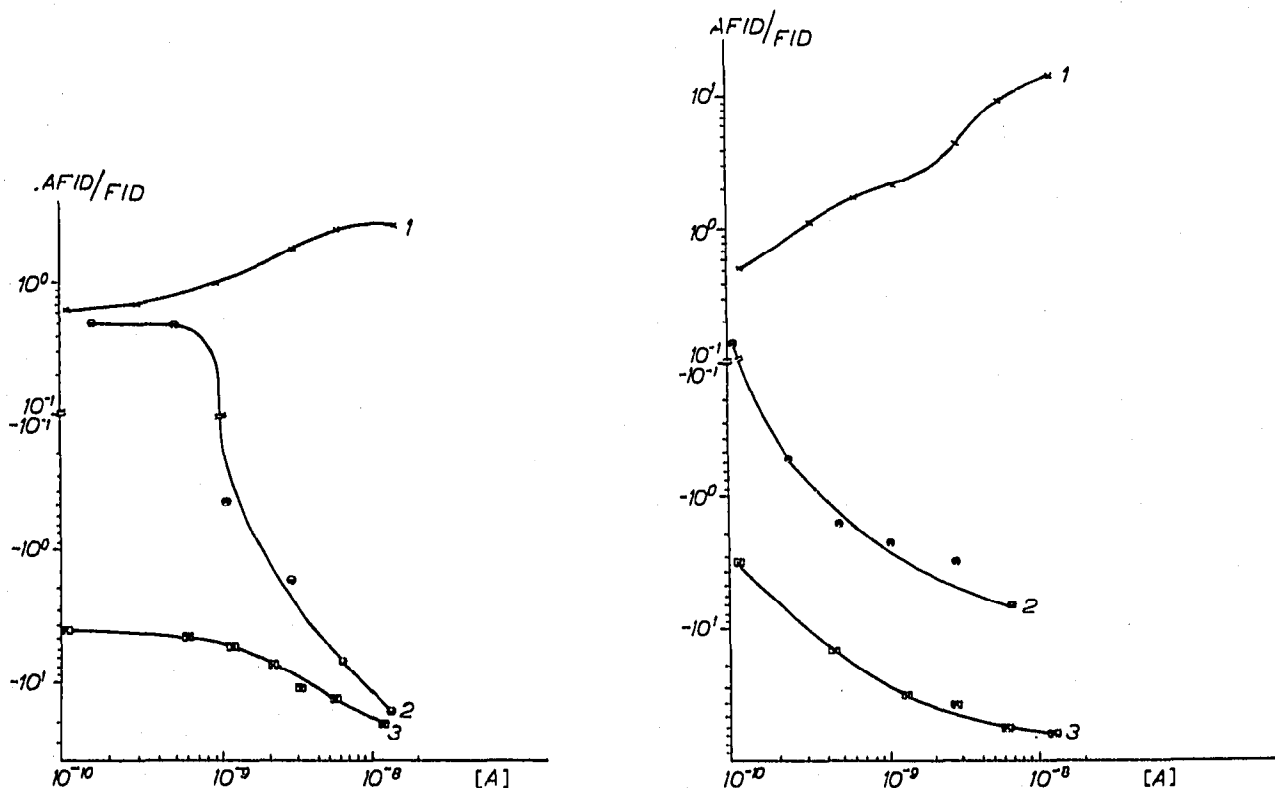


Fig. 1. Dependence of the response on the background current using a sodium salt. 1 = Trithoxysilane; 2 = tetraethyllead; 3 = tetraethyltin.

Fig. 2. Dependence of the response on the background current using a potassium salt. 1 = Trithoxysilane; 2 = tetraethyllead; 3 = tetraethyltin.

The response of the AFID to silicon compounds is thus selective for all the alkali metals in the sense of the response increase, when compared with that of the FID, as in the case of the AFID response to phosphorus and nitrogen compounds<sup>7</sup>. The AFID response to tin and lead compounds is selective not only in the sense of the response increase in contrast to the FID but also in polarity. The value of the background current at which the change in response polarity occurs depends on the type of the alkali metal employed and is, similar<sup>7,8</sup> to the case with sulphur and halogen compounds, the lower, the higher the atomic number of the alkali metal.

In order to compare the molar responses of the AFID used, the ionisation efficiencies at  $6 \times 10^{-9}$  A of all the elements studied are given in Table I. The response is obviously the highest in the case of the sodium salt for phosphorus compounds and decreases for the compounds of the individual elements in the following sequence  $P > Si > Br > Cl > I$ . The response to all these compounds is positive. A negative response is only found with this alkali metal to lead and tin compounds. With the use of sodium and background current  $6 \times 10^{-9}$  A the response of the detector to nitrogen and sulphur compounds is not selective and its value is somewhat lower than that of the FID. The highest response with potassium salt is again to phosphorus compounds and decreases further in the following sequence of elements  $P > Si > N > I$ . Negative response increases in the sequence of the compounds of  $Pb < S < Sn$ . The response of the detector to chloro- and bromo-compounds is, at this value of the background current, nonselective and again somewhat lower than that of the FID. However, it becomes selective at higher values of the background current when it is negative.

TABLE I

IONISATION EFFICIENCY OF THE COMPOUNDS CONTAINING DIFFERENT ELEMENTS

Compound	Element	Ionisation efficiency (C/mole)	
		Na	K
DIP	P	$2.2 \times 10^2$	$3.5 \times 10^2$
Pyridine	N	—	$3.7 \times 10^0$
Triethoxymethylsilane	Si	$1.9 \times 10^0$	$6.7 \times 10^0$
Bromobenzene	Br	$1.9 \times 10^0$	—
Chlorobenzene	Cl	$1.1 \times 10^0$	—
Iodobenzene	I	$6.3 \times 10^{-1}$	$1.6 \times 10^0$
Thiophene	S	—	$-6.0 \times 10^0$
Tetraethyllead	Pb	$-3.7 \times 10^0$	$-4.2 \times 10^0$
Tetraethyltin	Sn	$-8.9 \times 10^0$	$-4.4 \times 10^1$

TABLE II

RETENTION VALUES OF TIN AND SULPHUR COMPOUNDS AND THEIR STANDARD DEVIATIONS

Compound	Retention value (mm)		$\sigma$ (mm)	
	FID	AFID	FID	AFID
Tetraethyltin	116.8	127.6	8.4	14.3
Thiophene	126.2	126.2	15.8	15.9

When following the AFID response to lead and tin compounds, certain anomalies in the shape of the chromatographic curve and retention data of these compounds were observed.

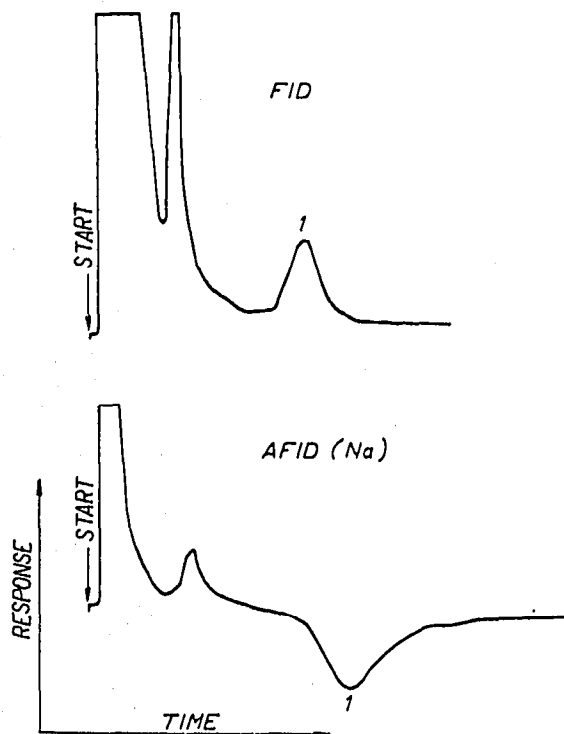


Fig. 3. Chromatograms of tetraethyltin.

The retention data and standard deviations of the chromatographic curves of tetraethyltin with the use of the FID and AFID are presented in Table II. All the chromatographic conditions were identical; in the case of the AFID the tip of the pressed salt of an alkali metal was only fixed to the jet of quartz glass. Both retention value and standard deviation are substantially higher with the AFID than with the FID. Similar differences were also obtained for tetraethyllead. The chromatograms of tetraethyltin with the use of the respective detectors are shown in Fig. 3. Thus it seems that a reaction takes place on the surface of the alkali metal salt. This conclusion is further supported by the fact that a black deposit can be found on the surface of the tip of the pressed alkali metal salt after repeated injections of large amounts of tetraethyllead or tetraethyltin. At the same time the background current decreases. The black deposit disappears after abrasion and the background current again acquires its original value. Another criterion supporting the above conclusion is the fact that the retention curves of lead and tin compounds do not decrease to the original baseline. This effect is very marked at high concentrations of lead and tin compounds.

In order to draw some general conclusions concerning the reaction on the surface of the alkali metal salt in the case of lead and tin, the influence of the use of the tip of the pressed alkali metal salt, *i.e.* comparison of the AFID and FID, was also investigated with respect to the retention volume and standard deviation of the retention curve of thiophene. Thiophene, as a sulphur compound, also has a negative

response in the case of potassium, rubidium and cesium. However, it is obvious from Table II that in this case changes neither in retention value nor standard deviation take place. The reason for the negative response to sulphur compounds apparently differs from the reason for the response to lead and tin compounds.

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