Short Communication

Potential variability problems with the alkali flame ionization detector used in gas chromatography

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ABSTRACT

Systematic gas chromatographic measurements on fourteen nitrogen- and three phosphorus-containing environmental pollutants revealed that potential variability problems may arise when using an alkali flame ionization detector. During an experimental period of 2 weeks the decrease in detector response turned out to be similar for homologous compounds, but different for compounds of diverse chemical classes. Although the absolute decrease in detector response may vary from bead to bead and, in addition, from one manufacturer to another, quantification appears to be feasable if this problem is taken into account by choosing internal standards of the same chemical class.

INTRODUCTION

Alkali flame ionization detection (AFID) is widely used in gas chromatographic analyses of environmental and pharmaceutical samples because of its unequivocal potential to detect and determine trace amounts of nitrogen- and/or phosphorus-containing organic compounds. This holds, in particular, for the trace analysis of pesticides such as triazine derivatives, *e.g.*, atrazine, and of industrially used organophosphates, *e.g.*, tri-*n*-butyl phosphate.

Although AFID is applied on a large scale and there have been many investigations on its function, the understanding of the detector is still poor [1–8]. It is assumed that pyrolysis of the

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analyte in the flame of the detector in the presence of alkali metal ions or excited alkali metal atoms gives rise to the formation of $CN^{-\bullet}$ and $PO_3^{-\bullet}$ species [6], which in turn lead to a sufficiently strong signal of the detector. However, these alkali metal sources, which are mostly installed as salt beads in a silicate matrix, are known to become exhausted [7]. Some beads are "consumed" more rapidly than others, which apparently is determined by how the bead is made. For example, Carlo Erba sources that were applied in this investigation are stated by the manufacturer to last for about 25 days [8]. As a consequence of this process, the signal response, *i.e.*, the peak area integral, of a given amount of analyte decreases with time. However, to the authors' knowledge, no systematic investigation has been reported that clarifies the question of whether the decrease in the signal

response is the same for all substances or whether it is different for each compound. This work was aimed at filling this gap.

EXPERIMENTAL

The experiments were performed with a Carlo Erba GC 6000 (Vega Series) gas chromatograph equipped with an AS 550 autosampler and an AFID system built by Carlo Erba (Milan, Italy). The gas chromatographic conditions were as follows: NB-54 column (25 m × 0.32 mm I.D., film thickness 0.25 μm) from Nordibond (Helsinki, Finland) (comparable to SE-54); on-column injection, with an injection volume of 2 μl containing 2 ng of each analyte; carrier gas, helium (98 kPa); detector temperature, 573 K (300°C); and detector gases, air (108 kPa), hydrogen (78 kPa) and make-up gas helium (70 kPa). The detector burned continuously during the experimental period of 2 weeks. The column temperature programme was initial temperature 343 K, increased at 5 K/min to 433 K (held for 20 min), then increased at 6 K/min to 523 K (held for 30 min).

4-Chloroaniline, tri-n-butyl phosphate, tri(2-methylpropyl) phosphate, triphenyl phosphate and ethyl acetate (analytical-reagent grade) as solvent were obtained from Merck (Darmstadt, Germany). The standard compounds propham, aldicarb, propoxur, cycloate, simazine, atrazine, propazine, terbuthylazine, pirimicarb, linuron, terbutryne, anilazine and flamprop-methyl were supplied by Promochem (Wesel, Germany).

During an experimental period of 2 weeks a standard solution containing all of the nitrogen- and phosphorus-containing compounds listed above was injected three times a day in order to test whether the decrease in the detector signal is a general or a substance-specific phenomenon. Each day, an average peak integral was calculated. At the end of the period, all integrals determined for one specific substance were normalized to the largest integral within the respective series of that specific compound.

The experiments were confined to 2 weeks instead of the complete lifetime of a salt bead (3 weeks) because we had to change the gas cylinder after that period. It is interesting that re-

ignition of the gas flame caused an additional significant effect on the detector response which also has to be taken into account when planning the analytical strategy over several weeks.

RESULTS AND DISCUSSION

It would be beyond the scope of this paper to show the plots for all seventeen compounds investigated. Further, it is not our intention to claim that the data are representative of all AFID sensors available on the market on an absolute scale. The absolute values would only apply to the Carlo Erba detector used. Therefore, we refrained from running a large number of beads, and confined ourselves to two repetitions. However, it should be noted that data from many additional runs, although not performed systematically (injections three times per day, over 2 weeks, etc.) are available that clearly support the present findings.

In general, the results show that substances of different chemical classes do not necessarily exhibit the same temporal decrease in detector response. As an example, typical graphs which are characteristic of atrazine, tri-n-butyl phosphate and aldicarb are shown in Fig. 1. The structures of these three compounds are given in Fig. 2. Whereas the signal response of tri-n-butyl phosphate decreased to about 40% of its original value within 2 weeks, the responses of atrazine
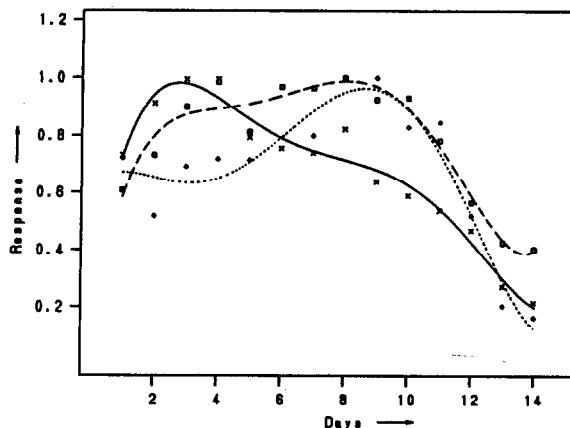

Fig. 1. Temporal decrease in AFID response to (×) atrazine, (□) tri-n-butylphosphate and (♦) aldicarb. The response was normalized to the maximum value for each compound.

and of aldicarb were reduced to about 25% within the same period. However, in the last two instances, the characteristics of the curves are significantly different; in particular, the position of the maxima and the slope are dissimilar. The signal responses of most compounds investigated exhibit characteristics comparable to one of the three substances displayed in Fig. 1; the curves for propazine, simazine, terbuthylazine, cycloate, pirimicarb, propham, propoxur, flamprop-methyl, linuron and terbutryne are comparable to that of atrazine, the curve for anilazine is comparable to that of aldicarb and the characteristics of the organophosphates resemble those of tri-*n*-butyl phosphate. Only the response of 4-chloroaniline shows a fourth characteristic deviating significantly from the other three curves.

At first glance, chemicals of the same class seem to cause similar responses to the detector. On the other hand, a comparison of the graphs for atrazine and anilazine shows that this observation should not be generalized. These results imply that caution must be exercised when using AFID for the determination of nitrogen- or phosphorus-containing compounds. The choice of an appropriate standard is obviously a crucial aspect. A necessary condition appears to be that the standard should belong to the same chemical class as the analyte, because it is difficult, if not impossible, to find one internal standard that shows the same detector responses as several phosphorus- and nitrogen-containing chemicals.

The present data can be generalized insofar as they reveal a potential problem with all AFID sensors, regardless of their specific performance characteristics such as within-day or day-to-day reproducibility. However, it will be impossible to determine a time function of the detector response for each analyte that is generally valid for more than one manufacturer. Therefore, it is recommended that recalibration with external standards should be performed every few days at least.
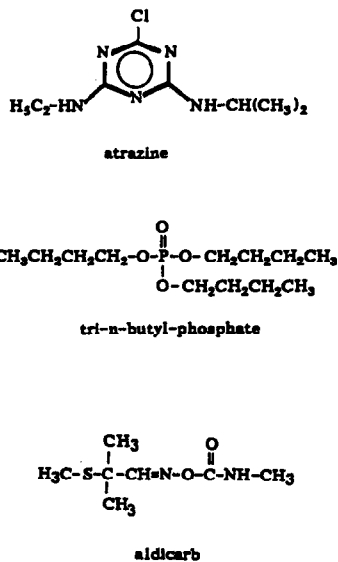
ACKNOWLEDGEMENT

Fig. 2. Structures of atrazine, tri-*n*-butyl phosphate and aldicarb.

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