Determination of some pesticides and intermediates by ion chromatography

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Abstract

We explored the possibility of determining some pesticides and process intermediates by ion chromatography. Some applications of this technique, standardized and adopted to meet the requirements of Gharda Chemicals (which is a leading producer of agrochemicals in India), will be presented in this communication. These include analysis of the finished products [(a) dicamba dimethylamine (DMA)/potassium/sodium salt acid and (b) 2,4-dichlorophenoxyacetic acid (2,4-D)], and the process intermediates [(c) tetrachlorobutyric acid and (d) glyoxylic acid/glycollic acid/formic acid]. Ion chromatographic analysis of sub-ppm levels of 2,5-dibromo- and monochlorobromo-phenols, in 2,5-dichlorophenol, after adequate sample preparation steps, is also being presented.   © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ion chromatography (IC) is an excellent technique for the quick and convenient determination of hydrophilic and ionic substances [1–7]. It offers improved speed, sensitivity, selectivity and simultaneous detection capabilities.

A literature survey indicated that this ingenious technique has found only limited applicability in the pesticide industry. For example, ion-exchange- and liquid chromatography with electrical conductivity detection have been recommended in the Collaborative International Pesticides Analytical Council Limited (CIPAC) Volume G for fosetyl–aluminium technical [8]. For the analysis of glufosinate ammonium, it is dissolved in an aqueous solution of potassium hydrogen phosphate and determined by HPLC with a strongly basic anion-exchange column and UV detection at 195 nm [9]. Chlormequat chloride techni-

cal concentrate is dissolved in water and determined by IC on a silica-based cation-exchange column using an acetone–water–ethylenediamine mixture as eluent, conductivity detection and external standardisation [10]. 2,4-Dichlorophenoxyacetic acid (2,4-D) and picloram aqueous solutions are analysed by HPLC on an ion-exchange column. Salicylic acid is used as an internal standard (UV detection at 280 nm) [11]. Glyphosate (technical grade) is also determined by ion-exchange chromatography (UV detection at 195 nm) using a strong anion-exchange resin. External standardisation is used for this analysis [12].

It appears that IC with conductivity detection has been applied to a very limited extent only, for pesticide-related analysis. In view of this, we decided to explore the applicability of IC with conductivity detection for various analyses required in the pesticide industry.

Some applications of this technique, standardized and adopted to meet the requirements of Gharda

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Chemicals, will be presented. These include analysis of the finished products (a) dicamba dimethylamine (DMA)/potassium/sodium salt and (b) (2,4-D), and the process intermediates (c) tetrachlorobutyric acid (which is a process intermediate in the cypermethrin process) (d) glyoxylic acid/glycollic acid/formic acid (which are intermediates in the metamitron process). IC analysis of sub-ppm levels of 2,5-dibromo- and monochlorobromophenols, in 2,5-dichlorophenol (in terms of the total bromide content), after adequate sample preparation steps, is also being presented. 2,5-Dichlorophenol is a process intermediate in the dicamba process. It may contain traces of bromine derivatives, based on the manufacturing process adopted. Bromine derivatives, even at trace levels, are considered as undesirable by-products in this process intermediate.

2. Experimental

2.1. Equipment

An IC system DX-500 from Dionex, USA,

equipped with a CD-20 conductivity detector and a self-regenerating suppressor facility and accessories was used for the investigations.

2.2. Reagents and chemicals

Chromatography-grade water was used to prepare all solutions. All reagents and chemicals used were of analytical reagent or equivalent grade. Reference standards used in these investigations were prepared in our Research and Development Laboratories. Their purities were ascertained by standard procedures.

2.3. Applications of IC at Gharda Chemicals

The general analytical conditions employed for the different IC experiments are given in Table 1. Some additional information, relevant to each investigation, is given below.

2.3.1. Assay of technical/formulated pesticides

(a) Dicamba–DMA/K/Na salt: A 50-mg amount

Table 1
Typical ion chromatographic analyses carried out at Gharda Chemicals[a]

No.	Analysis carried out	Column used	Suppressor used and suppressor current	Mobile phase used and flow-rate (in ml/min)	Internal standard used (anion)
1	Active ingredient in dicamba-dimethyl amine/dicamba–Na/dicamba–K salt formulations	A	B	C D	Sulphate
2	Active ingredient content in 2,4-dichlorophenoxyacetic acid technical	A	B	C D	Sulphate
3	Tetrachlorobutyric acid assay[b]	A	B	C D	–
4	Simultaneous estimation of glyoxalic acid, glycollic acid and formic acid[c]	A	B	E G	–
5	Traces of 2,5-dibromo- and monochlorobromophenols in 2,5-dichlorophenol in terms of total bromine content[d]	A	B	F D	–

[a] A=IONPAC AS4A-SC (250×4 mm); B=ASRS-I ultra, 4 mm; current=100 mA; C=1.8 mM Na$_2$CO$_3$ +1.7 mM NaHCO$_3$; D=1.0 ml/min; E=1 mM Na$_2$B$_4$O$_7$; F=10 mM Na$_2$B$_4$O$_7$; G=0.5 ml/min.

[b] Intermediate in the cypermethrin process.

[c] Intermediate in the metamitron process.

[d] 2,5-Dichlorophenol is an intermediate in the dicamba process. It may contain traces of bromine derivatives, depending on the process adopted. Bromine derivatives are undesirable by-products in this process intermediate.

of the sample was dissolved in 10 ml of the I.S. solution (5 mg/ml Na_2SO_4 in water). The solution was made up to 50 ml with water. A 2-ml volume of this solution was then diluted to 25 ml. A 20-μl volume of this final solution was injected into the IC unit (Fig. 1). (b) 2,4-Dichlorophenoxyacetic acid: A 50-mg amount of the sample was dissolved in 25 ml of the mobile phase (1.8 mM Na_2CO_3 +1.7 mM $NaHCO_3$), using sonication. A 5-ml volume of the I.S. solution (2 mg/ml Na_2SO_4 in water) was added and the solution was made up to 50 ml with water. A 2-ml volume of this solution was then made up to 25 ml and 20 μl of this final solution were injected into the IC unit (Fig. 2).

2.3.2. Assay of process intermediates

(a) Tetrachlorobutyric acid: This is an intermediate in the cypermethrin process. In this case, 50 mg of
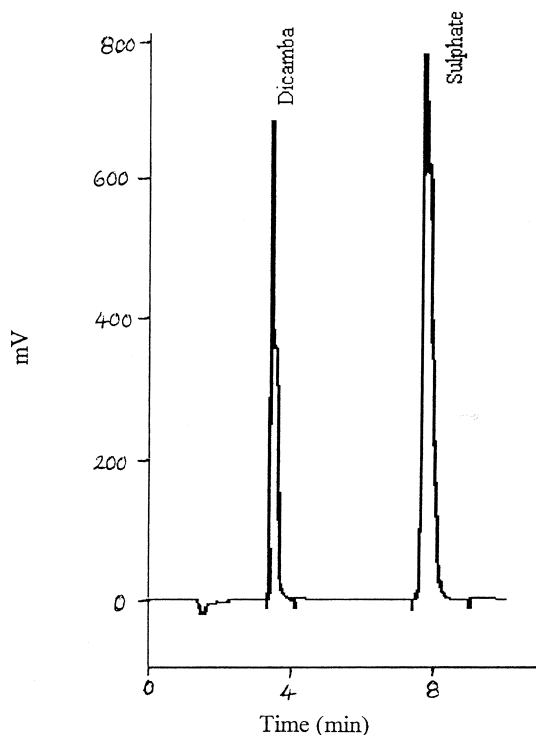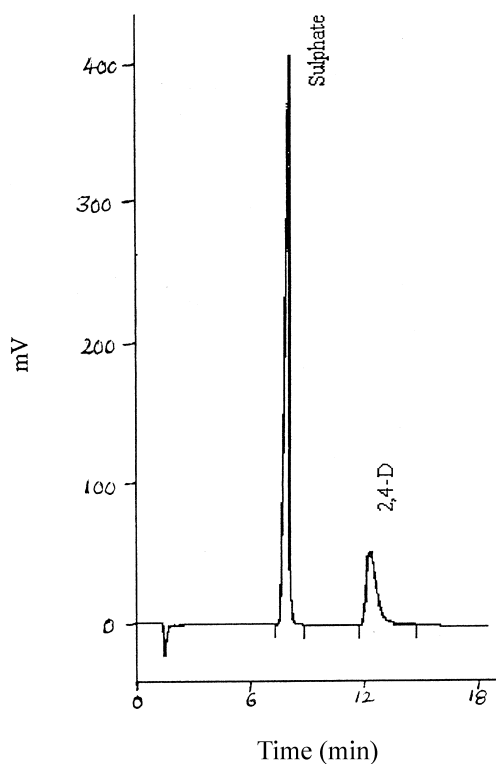
Fig. 2. Estimation of the active ingredient of 2,4-D. Chromatography conditions: column, IONPAC AS4A-SC (250×4 mm); suppressor, ASRS-I (4 mm) in autoregeneration external water mode, current=100 mA; mobile phase, 1.8 mM Na_2CO_3+1.7 mM $NaHCO_3$; flow-rate, 1.0 ml/min.

the sample were mixed with 25 ml of the mobile phase (1.8 mM Na_2CO_3+1.7 mM $NaHCO_3$) and dissolved using sonication. Finally, the solution was made up to 50 ml with the mobile phase. A 20-μl volume of this solution was injected for final analysis (Fig. 3). (b) Glyoxylic/glycollic/formic acid: These appeared together at an intermediate stage in the metamitron process. In this case, 50 mg of reaction mass were dissolved and diluted to 50 ml with water and 20 μl were injected into the IC unit (Fig. 4). (c) Traces of 2,5-dibromo- and monochlorobromophenols in 2,5-dichlorophenol: Bromine analogues are suspected trace/ultratrace impurities in 2,5-dichlorophenol, which is an intermediate in the dicamba process, depending on the process adopted. The bromo derivatives are undesirable by-products in this process intermediate. Their absence had to be confirmed before proceeding further with the process. For this purpose, 1 g of 2,5-dichlorophenol was

Fig. 1. Estimation of the active ingredient of dicamba–DMA/ dicamba–Na/dicamba–K salt. Chromatography conditions: column, IONPAC AS4A-SC (250×4 mm); suppressor, ASRS-I (4 mm) in autoregeneration external water mode, current=100 mA; mobile phase, 1.8 mM Na_2CO_3+ 1.7 mM $NaHCO_3$; flow-rate, 1.0 ml/min.
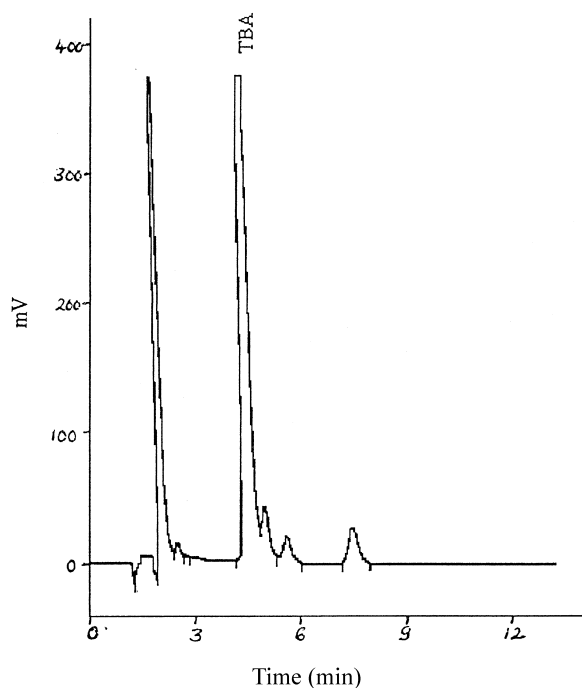
Fig. 3. Estimation of tetrachlorobutyric acid (TBA). Chromatography conditions: column, IONPAC AS4A-SC (250×4 mm); suppressor, ASRS-I (4 mm) in autoregeneration external water mode, current=100 mA; mobile phase: 1.8 mM Na$_2$CO$_3$+1.7 mM NaHCO$_3$; flow-rate, 1.0 ml/min.
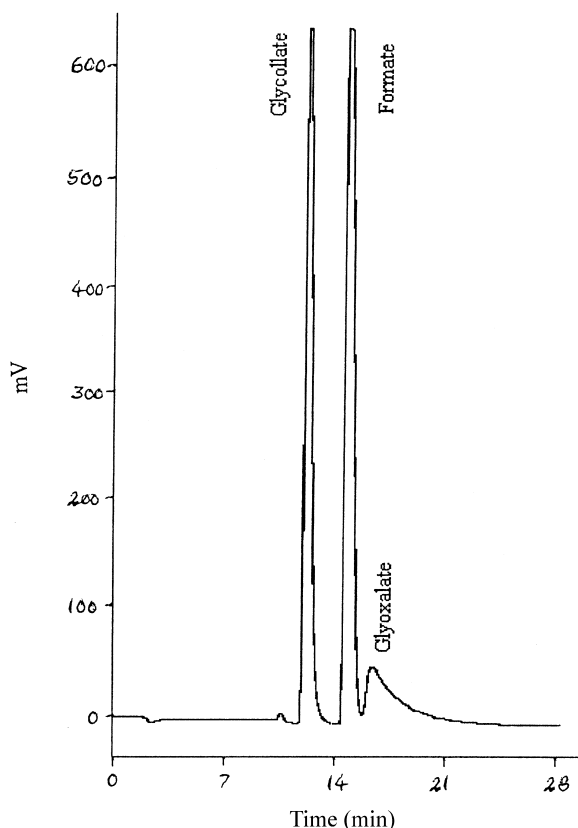

Fig. 4. Simultaneous estimation of formic acid, glyoxylic acid and glycollic acid. Chromatography conditions: column, IONPAC AS4A-SC (250×4 mm); suppressor, ASRS-I (4 mm) in autoregeneration external water mode, current=100 mA; mobile phase, 1 mM Na$_2$B$_4$O$_7$; flow-rate, 0.5 ml/min.

dissolved in 100 ml of toluene and transferred to a 500-ml separating funnel. To the toluene solution, sodium biphenyl reagent (0.5 M) was added slowly, with continuous swirling. The addition was continued until a dark bluish–green colour persisted, due to excess sodium biphenyl. The mixture was shaken thoroughly to ensure complete reaction, and excess sodium biphenyl was destroyed by adding water very slowly, avoiding excess heating of the mixture due to exothermic reaction. On destruction of the dark green colour, the mixture was thoroughly shaken to extract sodium chloride and bromide into the aqueous layer. The aqueous layer was separated, acidified with 10% nitric acid solution and treated with 5 ml of 0.1 M silver nitrate solution, to precipitate AgBr and some AgCl. The precipitate was filtered off and dissolved in liquor ammonia and made up to 50 ml with the same. This ammoniacal solution was analysed for bromide anion content (Fig. 5) using IC.

3. Results and discussion

Gas–liquid chromatography (GLC) is the preferred method for pesticide analysis. However, in the case of the compounds discussed in this work, it would not be a suitable technique to adopt. The reason is that the first set of analytes are salts of an acid while all others are acids. Unless one goes for derivatisation, successful analytical results cannot normally be obtained. Hence, GLC does not appear to be a good method for the analysis of these compounds. Either HPLC or IC seem to be the obvious choice.

A brief write-up on the compounds discussed in this work is given below. Dicamba is a herbicide
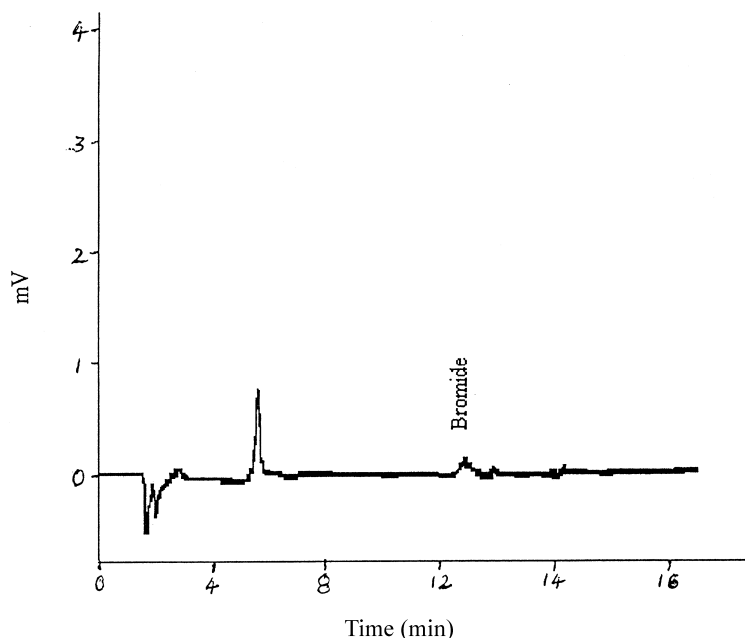
Fig. 5. Estimation of traces of 2,5-dibromo- and monochlorobromophenols in 2,5-dichlorophenol. Chromatography conditions: column, IONPAC AS4A-SC (250×4 mm); suppressor, ASRS-I (4 mm) in autoregeneration external water mode, current=100 mA; mobile phase, 10 mM Na$_2$B$_4$O$_7$; flow-rate, 1.0 ml/min.

used for controlling annual and perennial broad-leaved weed species in cereals, grain, maize, sugar-cane etc. 2,4-D is a systemic herbicide that is widely used for controlling weeds in cereals. Cypermethrin is a potent, broad-range insecticide that is effective against a wide range of pests and is used in citrus, cotton, rice, vegetables etc. Metamitron is a her-bicide with high selectivity to sugar and fodder beets, in which crops it is used to control broad-leaved and grass weeds.

The ion chromatograms obtained for the various samples are shown in Figs. 1–5. The operating conditions used for the various illustrations are summarised in Table 1.

So far as we know, there are no earlier references dealing with the application of IC for the assay of dicamba–DMA/K/Na salt. The method has been applied for the analysis of mixtures of 2,4-D and picloram aqueous solutions [11] (in various pro-portions). The authors have made use of a labora-tory-made Zipax SAX strong anion-exchange col-umn (100 cm×2.1 mm) without a suppressor. A UV detector was used at 280 nm. Using a single internal

standard (salicylic acid) and a mixture containing 0.01 M Na$_2$B$_4$O$_7$·10 H$_2$O and 0.002 M NaClO$_4$·H$_2$O as the mobile phase, both 2,4- D and picloram were estimated.

Fig. 1 shows the chromatogram of dicamba anion in the dicamba–DMA/K/Na salt finished product. Sulphate (from sodium sulphate) was used as the I.S. for this estimation. The IC method offers a number of advantages over the other methods (IR method recommended for the DMA salt [13] and the re-versed-phase HPLC method recommended for the estimation of dicamba in a mixed formulation [14]). For example, unlike the IR method recommended for dicamba–DMA aqueous solutions by CIPAC [14], the IC procedure involves separation prior to estima-tion. Better reliability and specificity can thus be obtained by this procedure compared to the IR method.

The I.S. method has been tested over a range from 70 to 130% of the mass of dicamba anion chosen for analysis (i.e. 35 to 65 mg of dicamba). It was found to be linear. The method is very specific and no interference from other related species was seen.

Repeatability of the method is 0.8% at the 990 g/kg level of dicamba.

In reversed-phase HPLC (recommended for mixtures of pesticides containing dicamba) determination of dicamba, very acidic buffers are recommended. These stringent conditions tend to reduce the column's life.

In the case of 2,4-D (Fig. 2), the I.S. method (using sulphate from sodium sulphate) was utilised for the estimation of the content of active ingredient. This approach makes use of the conductivity detector and the estimation is aimed not for the analysis of a mixture in which 2,4-D is a component. In the reversed-phase HPLC method (which is the normal procedure recommended for 2,4-D analysis) [15], acidic buffers are used, which reduce the life of the column. The I.S. method has been tested over a range from 70 to 130% of the mass of 2,4-D chosen for analysis (i.e., 35 to 65 mg of 2,4-D). The method is unsuitable for mixed formulations containing dicamba, as dicamba interferes with the 2,4-D peak. The repeatability of the method is 1.0% at 990 g/kg of 2,4-D.

There appears to have been no work done on tetrachlorobutyric acid using IC, and that too is a process intermediate in cypermethrin synthesis. Analysis was performed using the external standard method (Fig. 3), as it is only a process intermediate. The results obtained were more accurate than those obtained by the titrimetric method, since other acidic compounds will interfere in the latter case.

A survey of the literature reveals that Albarean and Collins [16] separated carboxylic acids (formic acid, oxalic acid, glyoxylic acid, glycollic acid and acetic acid) and simple non-ionic organic compounds using ion-modulated partition chromatography. There are also references in which individual acidic anions (among formate, glyoxalate and glycollate) have been separated and estimated in mixtures, using IC [17–19]. However, analysis of glyoxylic, glycollic acid and formic acid present together in a process intermediate of metamitron using IC has not been reported previously.

The ion chromatogram in Fig. 4 shows good separation of all anions of these three acids. It is possible to accurately estimate these anions in one IC run, when they are present together, using the external standard method. The simultaneous evaluation of all three components is a special attraction of the IC procedure. Titrimetry, the conventional method of analysis. will not be able to estimate all three acids separately.

Tetrachlorobutyric acid and a mixture of glyoxylic, glycollic and formic acids are process intermediates, so there is no need for their estimation with very great accuracy. Hence, the linearity of range and other checks were not carried out for these analyses.

An interesting application (IC using the external standard method) is for the estimation of trace (sub-ppm) levels of 2,5-dibromo- and monochlorobromophenols in 2,5-dichlorophenol (which is an intermediate in the dicamba process) by estimating the bromide anion after suitable sample work-up (Fig. 5). The estimation of traces of the bromine analogues of 2,5-dichlorophenol, through total bromine estimation by IC, illustrates how this approach can be extended and applied to even trace analysis of components in which an element of interest is present in a nonionic form. By appropriate chemical manipulations, the element is brought into an aqueous solution in an ionic form and is analysed by IC (external standard method).

In our case, the sample was dissolved in toluene and the bromide (and some amount of chloride) present in the compound was brought quantitatively into the anionic form by appropriate reactions with sodium biphenyl and subsequent extraction with water. The bromide and some amount of chloride were precipitated as silver halides. They were then dissolved in liquor ammonia and made up to 50 ml in volume. Using this method and the parameters employed, the limit of detection obtained using this procedure was 20 ng, which corresponds to 63 ng of 2,5-dibromophenol or 52 ng of chlorobromophenol (for 1 g sample of 2,5-dichlorophenol).

A 20-μl volume of the final solution containing the bromide and chloride anions was injected into the IC for the evaluation of the bromide formed. It is worth mentioning here that this test is extremely useful in confirming the absence of even sub-ppm levels of bromo derivatives in the 2,5-dichlorophenol. This is a very important step in the process of dicamba.

4. Conclusions

The analytical applications of IC have been used in a wide range of areas during the last two decades. However, the technique, especially with conductivity detection, has not yet found wide applicability in the pesticide industry.

In this work, we have highlighted some selected applications of IC in the pesticide industry. These include analysis of (a) finished products for their active ingredient contents and (b) process intermediates. IC analysis of sub-ppm levels of 2,5-dibromo and chlorobromophenol in 2,5-dichlorophenol, after adequate sample preparation steps, has also been covered. Mention can also be made about the utility in our organisation of IC for some environmental pollutants, some ionic impurities in boiler feed water, sulphur content in furnace oil and method of estimation of methane sulfonic acid using bromide as an internal standard.

Even though many of these analyses can be carried out by alternate procedures, IC turned out to be especially attractive, either because of the ionizable nature of the analyte species or the possibility of conversion of the analytes into ionizable species and the sensitive conductometric detector employed. The procedures developed offer speed, sensitivity, selectivity and simultaneous detection and analysis. In our considered opinion, there is ample scope to increase the application of IC in the pesticide industry.

We have preferred the use of the internal standard method for the determination of major components. Some earlier workers have also followed similar approaches [11,20].

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