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Capillary electrophoresis with detection by inverse UV spectroscopy and electrospray mass spectrometry for the examination of quaternary ammonium herbicides

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Abstract

The value of capillary electrophoresis (CE) and combined capillary electrophoresis–electrospray mass spectrometry (CE–ES-MS) for the analysis of simple quaternary ammonium ions, including herbicides, has been assessed. Choline, chlormequat, known contaminants of their formulation products, and some other small ammonium cations have been examined. Lacking a chromophore, the cations were detected by inverse UV absorption utilizing a buffer containing creatinine as visualization agent. In this way, all six cations could be resolved, detected and quantified within 8 min. To confirm the identities of the ammonium ions, coupled ES-MS provided mass measurement on all migrating cations. The triaxial probe proved to be an efficient interface for examining the small cations (m/z 60–124) by CE–ES-MS. Results on three formulation products containing chlormequat have been obtained by CE and CE–ES-MS, and compared with quantitative data from analysis by ion chromatography.

Keywords: Detection, electrophoresis; Environmental analysis; Mass spectrometry; Pesticides

1. Introduction

The high separation efficiency of capillary electrophoresis (CE) and its ability to accommodate many types of both large and small molecules makes it a highly desirable separation technique [1–3]. The standard visualization mechanism in CE is UV absorption although fluorescence detectors are also widely used. These direct spectroscopic approaches require analytes that contain a chromophore or fluorophore or that can be derivatized so as to impart such properties. However, detection of non-chromophoric compounds can also be facilitated by using spectroscopic methods in an indirect mode. The key to this latter approach is the displacement of a highly absorbing mobile phase additive in the buffer by the sample analytes. The spectroscopic signal is derived from this mobile phase additive rather than from the analytes themselves but the analytes are detected because the concentration of the chromophoric additive is lower in the eluted bands when compared with its steady state concentration [4]. This inverse photometric detection (IPD) has been applied to CE by Foret et al. [5] who

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studied the effect of ion mobility on peak shape and found that higher sensitivity was obtained with visualizing agents which had high molar absorptivity and mobilities similar to those of the sample ions. The closer the two mobilities could be matched, the better were the detection limits obtained, even if a compromise between the UV absorbance and the mobility of the visualising agent sometimes had to be made [6].

For analysis of non-chromophoric substances by CE, an alternative or additional strategy involves coupled mass spectrometry. The technique of electrospray mass spectrometry (ES-MS) can be used as an on-line detection method for the unambiguous identification of compounds as they elute from the end of a CE column. Like CE, ES-MS is used to analyse a wide range of compounds from very small to very large polar and ionic analytes in aqueous solution [7,8]. Hence, the two methods are compatible in terms of analyte range. The main consideration for the coupling of the two techniques is making consistent their two different flow-rates: nl/min in CE and μl/min in ES-MS. This discrepancy can be overcome by adding a make-up flow to the CE effluent prior to on-line ES-MS [8–11]. This flow dilutes the CE buffer sufficiently to allow additives such as those required for inverse UV detection to be used in the CE–ES-MS mode even though they may be involatile in comparison to conventional electrospray solvents.

In this work, two detection techniques that do not require a chromophoric analyte, inverse UV absorption and ES-MS, have been applied to the examination by CE of some aliphatic quaternary amine herbicides of environmental importance. Established methods of analysis of such formulated pesticides include potentiometric titration with silver nitrate, colorimetry and ion chromatography. Unfortunately, the titration and colorimetric methods are not satisfactory for the enforcement of environmental legislation (e.g. the Control of Pesticide Regulations, COPR). High-performance liquid chromatography has been used to examine similar compounds, also using IPD [12,13], including one of the compounds in our study, chlormequat [14], thus showing the feasibility of IPD in a different separative procedure. The technique of capillary zone electrophoresis itself cannot provide low enough detection limits for trace environmental samples but another form of CE, isotachophoresis, has successfully been used for the analysis of trace levels of such compounds [15]. In our work, however, the testing of formulation products is paramount and therefore the required limits of detection are not stringent and in fact the samples have to be diluted substantially before analysis. CE provides a fast and accurate method of analysis for these compounds and has advantages over ion chromatography in terms of speed and peak capacity. Other biologically important amines [16], inorganic cations [17–19] and anions [20] have also been analysed using IPD.

The herbicides considered in these studies are chlormequat chloride (**1**) and choline chloride (**2**) along with their known by-products, trimethylamine hydrochloride (**3**) and trimethylvinylammonium chloride (**4**). Their cations are shown in Fig. 1. The two herbicides are used to protect and enhance the ability of plants such as wheat and cotton to resist fungicidal infection and infestation. It is unlikely that they have a direct fungal or insecticidal action. Use of such compounds generally results in higher yields of the crops to which they are applied [21–24].

A fundamental difficulty in the analysis of these herbicides and their by-products is the lack of a useful chromophoric group within the cations. Hence, IPD and MS were applied here. The indirect spectroscopic method of detection has disadvantages in relatively poor limits of detection (e.g. there are often three orders of magnitude difference between

	Cation structure	Chemical name	Cation mass
1	$ClCH_2-CH_2-\overset{+}{N}(CH_3)_3$	Chlorocholine chloride (chlormequat)	122/4
2	$HO-CH_2-CH_2-\overset{+}{N}(CH_3)_3$	Choline chloride	104
3	$(CH_3)_3\overset{+}{N}-H$	Trimethylamine hydrochloride	60
4	$CH_2=CH-\overset{+}{N}(CH_3)_3$	Trimethylvinylammonium hydroxide	86
5	$(CH_3)_2CH\overset{+}{N}H_3$	Isopropylammonium glyphosate	60
6	$(C_2H_5)_3\overset{+}{N}-H$	Triethylamine hydrochloride	102

Fig. 1. Cation structures of the non-chromophoric herbicides, **1** and **2**, under investigation, along with expected by-products, **3** and **4**, and two internal standards, **5** and **6**.

conventional and inverse fluorescence detection [25]). An important factor which has to be optimized before adequate sensitivity can be achieved is that of the noise coefficient which is the ratio of the concentration fluctuation to the concentration of the visualisation agent [26]. Although electromigration injection may provide an analysis with greater sensitivity [6], it also introduces injection bias as the more highly charged molecules migrate onto the column much faster than those less highly charged [27]. Therefore in these studies hydrodynamic pressure injections were utilized. Once optimized, the use of an internal standard during the analysis has been shown to validate IPD in CE as a fully quantitative method [28]. This, along with the determination of relative molecular mass and structural specificity offered by ES-MS, should provide an adequate method for the analysis of these herbicides. A major obstacle in the application of ES-MS to the cations in Fig. 1 concerns the very low masses of the cations under examination (m/z 60–124). Conventionally, such ions would be deemed inappropriate for ES-MS which generally shows much chemical background, due mainly to the solvent and solvent clusters, below m/z 150.

2. Experimental

2.1. Chemicals

The herbicide samples were supplied by the Health and Safety Laboratory (an agency of the Health and Safety Executive, HSE). All other chemicals used were obtained from commercial sources at the highest purity possible. Trimethylvinylammonium hydroxide (M_r 103.2) was used in place of its chloride (M_r 121.6) because only the former could be obtained in sufficient purity. Only the cation is detected by the CE method so, to calculate the concentration of the chloride in formulation products, the quantitative result determined by using the hydroxide as standard was corrected by the factor 121.6/103.2.

2.2. Instrumentation and methods

A Beckman P/ACE 2000 CE instrument was used for stand-alone CE. This instrument is equipped with a positive reversible power supply, coupled to an IBM-compatible integrator. Inverse UV detection was performed using a deuterium lamp with a 200-nm optical filter. Normal untreated silica capillaries of 50 μm internal diameters with a length of 70 cm to the detector window (80 cm total length) were utilised for the separations. Capillary columns were rinsed with 0.1 M NaOH for 2 min between each run followed by a 3-min rinse with the run buffer before separation at 25 kV and 25°C. The areas of the inverted peaks were measured by cutting them out and weighing them.

The buffer used for CE and CE–ES-MS was 10 mM creatinine made to pH 3.6 with ethanoic acid. With +30 kV applied across the capillary, this buffer gave rise to a current of 4.8 μA. Samples were introduced on column using 5-s hydrodynamic pressure injections resulting in the application of 5 nl of sample onto the column.

The analytical solutions used were all made up to contain triethylamine at the level of 100 μg/ml as internal standard. At the working pH, this standard migrated as its ammonium ion.

For CE–ES-MS studies, a Beckman P/ACE 2100 CE system fitted with a Beckman mass spectrometer interface was coupled to a VG BioTech Platform single quadrupole mass spectrometer equipped for electrospray via a triaxial flow probe interface (see Fig. 2). The CE separations were performed in a fused-silica capillary, 90 cm×375 μm O.D.×50 μm I.D., extending to the tip of the VG triaxial flow probe. The whole apparatus was kept at the same height to avoid siphoning effects. During the process of interfacing these two techniques it was found that the distance that the capillary tip protruded from the end of the triaxial probe was key to the resolution and reproducibility of the CE–ES-MS process. The arrangement of the surrounding stainless-steel tubing was similarly vital to performance. The capillary needed to protrude by about 1 mm, and no more than 5 mm, from the end of the stainless-steel sheath tube which in turn protruded by 0.5–1.0 mm from the external probe casing. All three tubes were kept as concentric as possible to avoid any flow disturbances. The experimental design at the probe tip is also shown in Fig. 2. The end of the capillary tube needed to be cut flush with no jagged edges to ensure

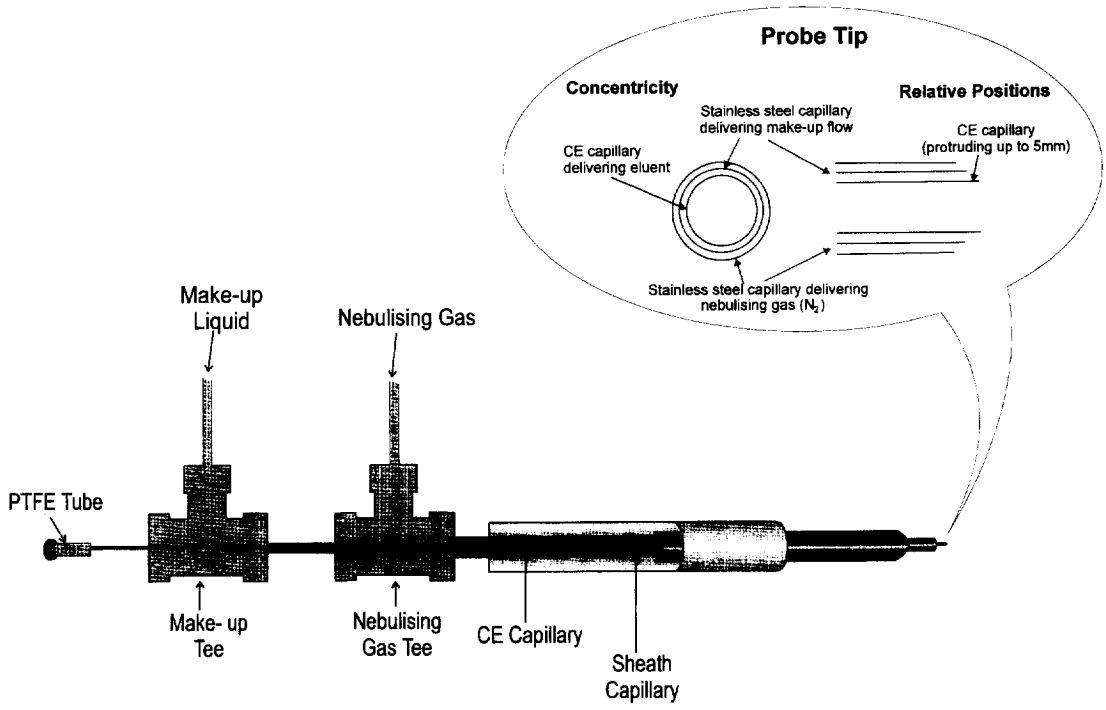


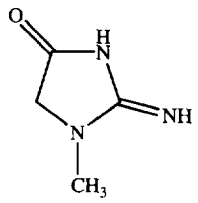
Fig. 2. Schematic diagram of the triaxial probe for coupling capillary electrophoresis to electrospray mass spectrometry. A schematic of the arrangement at the tip of the CE–ES-MS is inlaid.

an even flow of make-up solution and nebulising gas around the capillary tip where the buffer and analyte mixture eluted. Small adjustments were made to all these parameters until the best set of results was obtained. Monitoring the abundance and stability of the signal due to $[M+H]^+$ ions produced by creatinine (m/z 114) in the run buffer enabled electrospray performance and mixing of the flows at the probe tip to be assessed and optimized.

A window for UV absorbance detection was placed 20 cm from the point of injection. To assist electrospray, a make-up flow of methanol–water (50:50) acidified with 1% formic acid was delivered to the probe tip at 20 μl/min where it mixed with the CE buffer. This mixture is then nebulised using nitrogen gas which flows coaxially up the probe. A potential of +4 kV was applied to the probe tip for optimal electrospray performance, resulting in a decrease in the CE current. Mass spectral data were acquired using selected ion recording (SIR; 0.2 s dwell time, 0.2 u span). Six different ions were monitored (m/z 60, 86, 102, 104, 122 and 124) in a cyclic manner every 1.2 s. Acquisition of data was initiated shortly after the peaks had passed the UV window. Therefore, the scales of migration times associated with the CE–ES-MS traces shown below are not reproducible and not directly comparable with those given in the CE electropherograms in which injection is defined conventionally as zero time.

3. Results and discussion

The choice of visualization agent for inverse UV detection in these studies proved very important and the eventual use of creatinine, **7**, (see Fig. 3) follows the criteria established in other studies [29,30]. The requirement that the migration rates of the compounds to be analysed and that of the visualization agent are similar largely dictated the final choice. This similarity of migration rates was essential to ensure that the sample components migrate as symmetrical zones [30]. Creatinine also has a similar



7 Cation mass = 114

Fig. 3. Structure of creatinine, **7**.

structure and relative molecular mass to the herbicides and standard ammonium ions being examined which, coupled with its high absorbance at 200 nm and excellent buffering capacity, makes it an ideal choice for this work. As low concentrations of creatinine (10 m*M*) provide adequate CE separation, any possible complications that using such an involatile buffer may cause when coupling CE with ES-MS are minimised.

First, a mixture containing the two herbicides, the anticipated by-products and two internal standards, isopropylammonium glyphosate and triethylamine hydrochloride, was subject to CE. Under acid conditions (pH 3.6) each substance analysed is a quaternary ammonium ion and does not contain a useful chromophoric group (Fig. 1). During CE, as each cation passed the UV window, there was a reduction in the background absorbance of the highly chromophoric creatinine in the buffer. An inverse

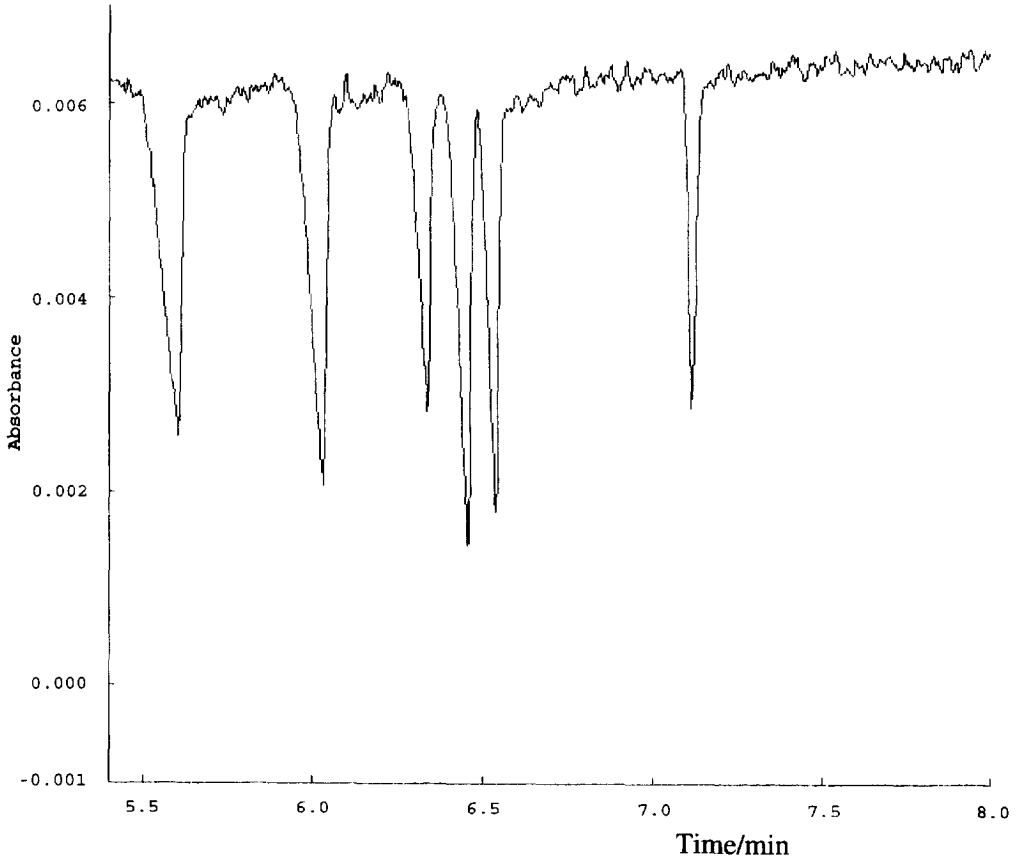


Fig. 4. Part of the inverted electropherogram obtained by analysing the ammonium ions shown in Fig. 1 by CE. Buffer: 10 m*M* creatinine made up to pH 3.6 with ethanoic acid; column: 70 cm×50 μm I.D.; separation at 25 kV at 25°C; detection: inverse UV absorption at 200 nm. In order of migration, the cations detected are: trimethylammonium, trimethylvinylammonium, isopropylammonium, choline, chlormequat and triethylammonium ions. The trace was obtained by introducing into the column 5 nl of a solution containing 100 μg/ml of each component.

UV electropherogram showing the separation of all of the components in the mixture is illustrated in Fig. 4. Each compound of interest is analysed as a small ammonium cation which, despite the low electro-osmotic flow produced at this pH, ensures that migration through the column is relatively fast: about

Table 1
Reproducibility: migration times for six consecutive injections of the ammonium ion mixture

Repetition number	Peak identity and migration time (min)					
	A	B	C	D	E	F
1	5.612	6.041	6.347	6.549	6.464	7.129
2	5.603	6.036	6.342	6.535	6.455	7.115
3	5.603	6.031	6.337	6.535	6.455	7.114
4	5.603	6.031	6.333	6.535	6.450	7.105
5	5.603	6.031	6.333	6.530	6.450	7.103
6	5.603	6.026	6.328	6.526	6.446	7.098

Sample mixtures containing analytes A–F each at 100 μg/ml were used: A=trimethylamine hydrochloride, B=trimethylvinylammonium hydroxide, C=isopropylammonium glyphosate, D=choline chloride, E=chlormequat chloride, F=triethylamine (migrating as its ammonium cation).

Table 2
Reproducibility: peak areas for six consecutive injections of the ammonium ion mixture at 100 μg/ml per component

Repetition number	Trimethyl-ammonium chloride	Trimethylvinyl-ammonium hydroxide	Isopropyl-ammonium chloride	Choline chloride	Chlormequat chloride
1	2.036	2.126	1.275	1.793	1.459
2	2.019	2.206	1.263	1.910	1.545
3	2.180	2.341	1.445	1.900	1.493
4	2.048	2.307	1.329	1.737	1.478
5	2.139	2.305	1.417	1.821	1.551
6	1.938	2.194	1.449	1.925	1.449
R.S.D (%)	4.2	3.7	6.2	4.1	2.9

The areas were calculated by cutting out and weighing the inverted peaks in grammes. The areas were corrected for any differences in the injection of each sample by dividing each mass by the mass of the sixth peak, due to a fixed concentration (100 μg/ml) of the internal standard, triethylamine.

Table 3
Peak area data obtained for the construction of calibration curves of the ammonium ions

Standard amounts (μg/ml)	Trimethyl-ammonium chloride	Trimethylvinyl-ammonium hydroxide	Isopropyl-ammonium chloride	Choline chloride	Chlormequat chloride
100	1.213	1.144	1.361	0.800	0.733
90	1.027	1.020	1.252	0.716	0.678
80	0.898	0.902	1.090	0.611	0.563
70	0.771	0.814	0.963	0.580	0.548
60	0.665	0.679	0.760	0.460	0.434
50	0.616	0.573	0.668	0.379	0.369
40	0.459	0.486	0.579	0.310	0.314
30	0.331	0.342	0.456	0.270	0.255
20	0.256	0.250	0.282	0.189	0.146
10	0.133	0.128	0.143	0.058	0.079
5	0.078	0.069	0.083	0.0285	0.041

The areas were calculated by cutting out and weighing the inverted peaks in grammes. The areas were corrected for any differences in the injection of each sample by dividing each mass by the mass of the sixth peak, due to a fixed concentration (100 μg/ml) of the internal standard, triethylamine.

Table 4
Capillary electrophoresis of chlormequat formulation products: the concentrations were measured in g/100 cm^3 (% w/v)

Sample number	Chlormequat chloride (% w/v)	Trimethylammonium chloride (% w/v)	Trimethylvinyl-ammonium chloride (% w/v)
71 692	39	4.8	5.7
30 665	53	5.7	6.7
30 660	58	7.0	8.0

Table 5
Ion chromatography of the chlormequat formulation products in Table 4: the concentrations were measured in g/100 cm^3 (% w/v)

Sample number	Chlormequat chloride (% w/v)	Trimethylammonium chloride (% w/v)	Trimethylvinyl-ammonium chloride (% w/v)
71 692	51±5	5.5±0.4	5.4±0.2
30 665	48±9	5.8±0.2	6.0±0.2
30 660	50±1	5.6±0.1	5.0±0.2

10 cm/min. Separation is completed to baseline throughout but a definite gradual improvement in peak width and symmetry is visible between the first peak (trimethylammonium ions; asymmetry ratio= 0.23; number of theoretical plates, n=54 000) and the last peak (triethylammonium ions; asymmetry ratio=1.0; n=513 000). The migration order was established by comparison of migration times of the individual compounds when analysed singly.

CE is known to provide highly reproducible results in the direct detection mode and before proceeding with the current analysis, reproducibility

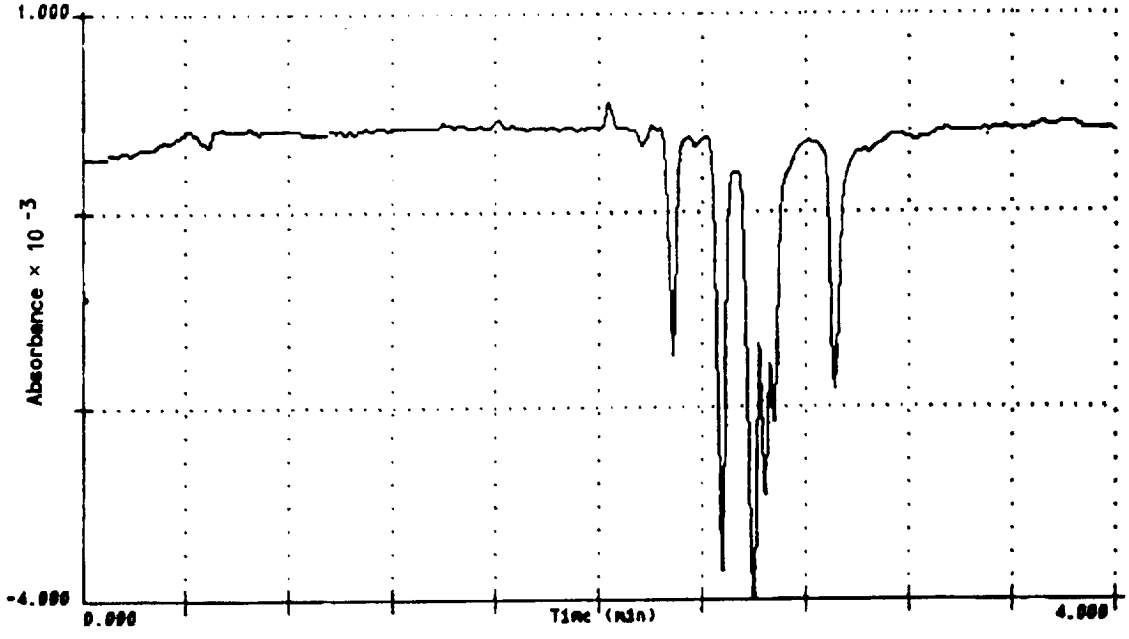


Fig. 5. Inverse UV detection of the six ammonium ions shown in Fig. 1, after migrating for 20 cm in a coupled CE–ES-MS system. The capillary electrophoresis conditions were those given in the legend to Fig. 4 except that the complete length of the capillary was 90 cm and the potential difference across the column was 21 kV. The order of migration is exactly the same as given in the legend of Fig. 4.

data were obtained for six consecutive injections. Reproducibility was measured for both migration times and peak areas and the results of these are shown in Table 1 and Table 2. The method was appropriate for qualitative work because relative standard deviations of less than 0.2% for migration times were obtained. In assessing the potential for quantitative analysis, relative standard deviations of less than 6.3% for peak area were noted.

For each constituent of the mixture, a calibration graph was derived. The data in Table 3 were collected using the same ammonium ion mixture as before but with a range of concentrations from 5 to 100 μg/ml per component. Again, the area of each peak was corrected via the internal standard. Calibration curves were constructed for each compound and the results expressed as scatter graphs. All of the plots were linear and their correlation coefficients were all above 0.99 which suggests that quantitative as well as qualitative results were valid. Typically, the signal-to-noise ratio was 3 at a concentration of 5 μg/ml. Therefore the limits of detection for all of the ammonium ions in this CE study by inverse UV detection were about 5 μg/ml.

The CE method was applied to the analysis of authentic concentrated formulation samples. These samples were thought to contain chlormequat and its by-products, trimethylammonium and trimethylvinylammonium chloride salts. The samples were diluted and then injected under the same conditions as for the standards above. Three inverted peaks were observed at the same migration times as for chlormequat, trimethylammonium and trimethylvinylammonium ions. The peak areas were measured and compared with the calibration curves to give a value for each analyte. After considering

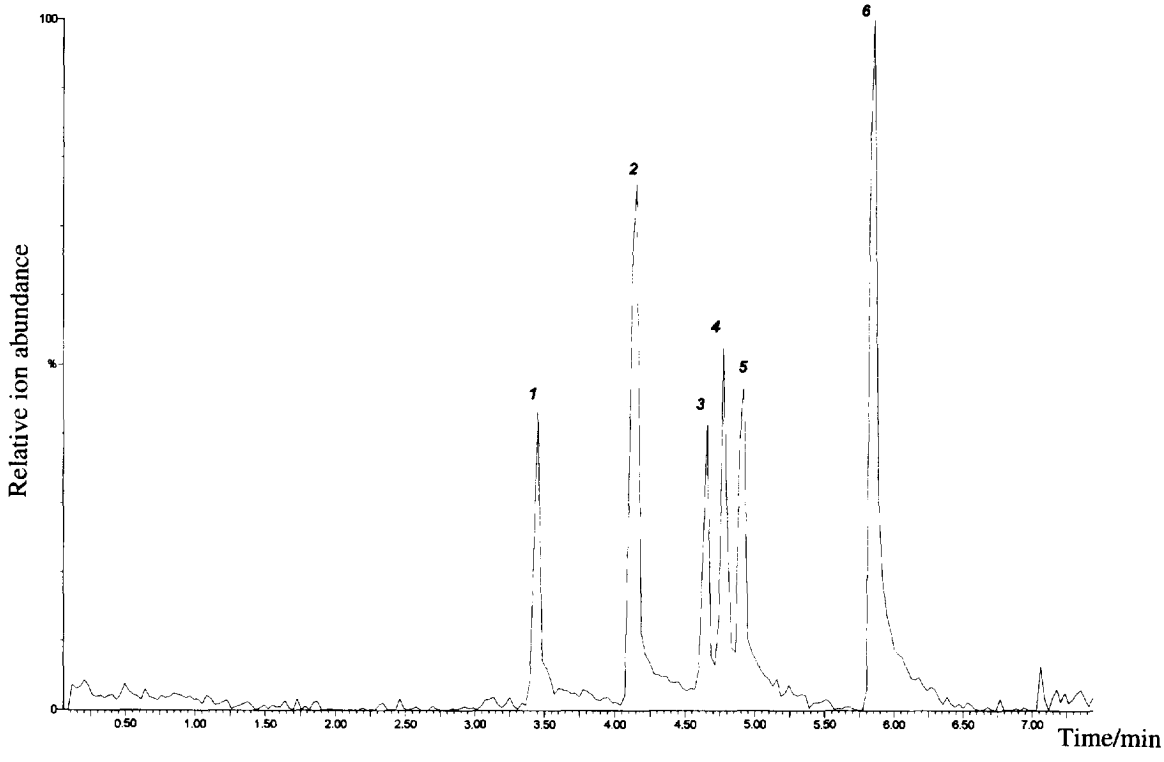


Fig. 6. The summed ion current trace for the analysis of the six ammonium ions shown in Fig. 1, after migrating 90 cm in a coupled CE–ES-MS system. Peak identities: 1=trimethylammonium ion; 2=trimethylvinylammonium ion; 3=isopropylammonium ion; 4=choline; 5=chlormequat; 6=triethylammonium ion. (Acquisition of data was begun after the components had passed the UV window at 20 cm, so the migration times on this trace are not comparable with those given in other figures.)

the dilution factors (and, in the case of trimethylvinylammonium chloride, correcting for the difference in mass between the hydroxide standard and the chloride analyte), the concentrations in the formulation product were derived (Table 4).

These results compared favourably with those obtained by the HSE using ion chromatography (Table 5). The formulation samples were very concentrated and had to be diluted 2000 or 10 000 times before analysis in order to bring the ammonium ion concentrations within the calibrated range. The method successfully identified the analytes in the real samples as chlormequat and its suspected by-products, and quantified them, thereby supplying important information on these samples which could be of use in the enforcement of relevant legislations.

The CE–ES-MS system was also used to analyse firstly the standard herbicide mixture, with each component at a concentration of 100 μg/ml, and then the formulation products. Fig. 5 is an electropherogram of the separation of the standard ammonium ions, detected by inverse UV absorption after 20 cm from the capillary inlet as they migrated towards the electrospray source. Full separation had not been achieved at this point. The selected ion recording (SIR) electropherogram (Fig. 6) shows the final resolution of the mixture containing about 3 pmol of each compound achieved after separation along 90 cm of the capillary. The plot shown in Fig. 6 is a summation of the individual selected ion current profiles taken from the SIR acquisition at six different m/z values. In this CE–ES-MS experiment, the separation number (Trennzahl, TZ) between the first and second eluting ammonium ions was estimated to be 2.2 after 20 cm and 4.6 after 90 cm of migration. This degree of resolution is comparable to that obtained for CE alone with an effective sepa-

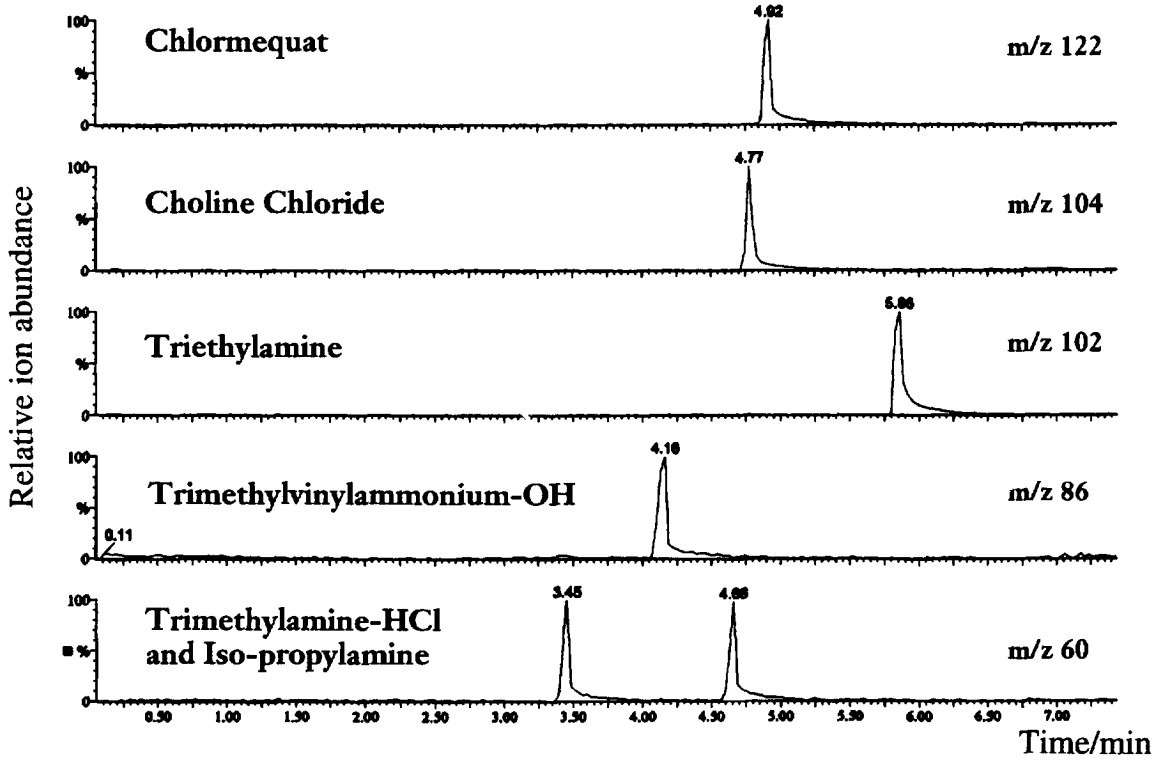


Fig. 7. The electropherogram shown in Fig. 5 reproduced as individual selected ion recordings. Comparison with the masses quoted in Fig. 1 allows confirmation of the identity of each ion (apart from trimethylammonium and isopropylammonium ions which have the same mass).

ration length of 70 cm (TZ=3.0). It may be concluded that the coupling of the mass spectrometer did not adversely affect CE separation.

The presence of creatinine in the buffer allowed the electrospray mass spectrometer to be tuned using the peak for its protonated molecule at *m/z* 114. It was assumed that the presence of creatinine would not have a significant effect on the detection of the quaternary ammonium ions by ES-MS. The results of the analysis, expressed as individual selected ion recordings (Fig. 7), reflect the fact that both isopropylammonium and trimethylammonium cations have the same mass (*m/z* 60). In addition, chlormequat gave two peaks (*m/z* 122 and 124) in a 3:1 ratio due to the presence of one chlorine atom. For simplicity, only the former is shown in Fig. 7. The elution order of the cations was established by mass spectral interpretation of these findings and by reference to the known migration behaviour determined by capillary electrophoresis alone (as above). Despite the fact that substantial solvent peaks occur in the low mass range in ES-MS, detection and measurement of the ammonium ions in this study (having masses in the range *m/z* 60–124) was not hampered by background signals.

Fig. 8 gives the CE–ES-MS data obtained on a formulation sample of chlormequat (sample 71692 as in Table 4). The purpose of the analysis was to establish the purity of the sample. The trace shown in Fig. 8 is the summed plot of all of the individual selected ion recordings that produced a response. Only signals at *m/z* 60, 86, 122 and 124 were detectable. Thus, the MS result confirms that the sample is impure, containing small amounts of trimethylammonium and trimethylvinylammonium cations as well as chlormequat. This qualitative result confirms the results obtained by CE alone, as given in Table 4 above.

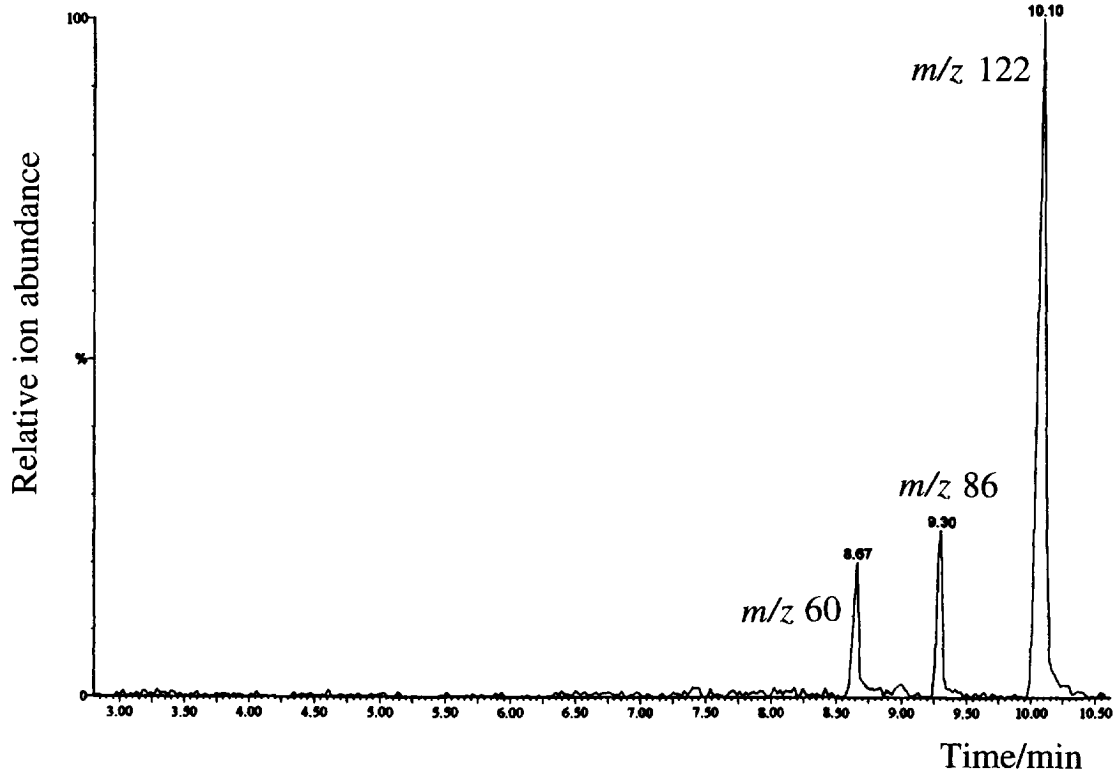


Fig. 8. Analysis by CE–ES-MS of the chlormequat formulation which gave the quantitative CE results shown in Table 4. The trace confirms the identities of the three components (i) trimethylammonium ions at *m/z* 60, (ii) trimethylvinylammonium ions at *m/z* 86, and (iii) chlormequat at *m/z* 122 (and *m/z* 124).

4. Conclusions

Simple non-chromophoric ammonium ions, including the herbicides chlormequat and choline, can be detected and quantified by CE by using inverse UV absorption with creatinine in the carrier buffer. Levels down to 5 μg/ml are readily measured. Despite the low mass of the eluting ammonium ions, the identity of each can be confirmed by combined CE–ES-MS using a triaxial probe as an interface.

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