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Contaminant and Formulation Analysis of MSMA using High-Pressure Liquid Chromatography – Graphite Furnace Atomic Absorption Spectrophotometry

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ABSTRACT

High-pressure liquid chromatography with an ion-exchange column combined with graphite furnace atomic absorption spectrometry was used to analyse commercial formulations of sodium hydrogen methylarsonate (MSMA). No arsenite or arsenate salts or dimethylarsinic acid were detected as contaminants in the formulations, and the MSMA concentrations were found to be in accordance with the concentrations given on the containers.

1 INTRODUCTION

The analysis of organoarsenical herbicide formulations mostly follows the principle of acid–base titration, with total arsenic being determined by wet oxidation.[1] This method does not, however, distinguish between different arsenical compounds which may be present as contaminants in a formulation. Residues of arsenical pesticide compounds have been separated by high-pressure liquid chromatography (h.p.l.c.) using a low capacity anion-exchange column, and the eluants then analysed by graphite furnace atomic absorption spectrophotometry (g.f.a.a.).[2] This principle was also used for the separation and analysis of arsenical compounds in environmental matrices.[3,4]

No reference to the separation and analyses of different arsenical contaminants in arsenic-based pesticide formulations could be found in available literature sources. In the work reported here, h.p.l.c. separation and g.f.a.a. analysis of three possible arsenical contaminants and of sodium hydrogen methylarsonate (MSMA) was investigated by a method very similar to that used by Woolson.[4] The

method was applied for contaminant analysis of different commercial formulations of the herbicide MSMA. MSMA is extensively used to control *inter alia* jointed cactus in the Republic of South Africa, and a number of formulations are supplied by different manufacturers.[5] Concern was expressed about the possibility of extensive farming areas becoming contaminated with highly-toxic inorganic arsenical compounds, and contaminant analysis of the formulations therefore became a matter of urgency.

2 EXPERIMENTAL METHODS

2.1 Equipment and materials

A Hewlett Packard 1082B h.p.l.c. equipped with a 100×8 mm diameter radial compression column (Waters Associates Inc.) packed with an anion-exchange resin (Biorad Aminex A-27) was used. A fraction collector (LKB 2111 Multirac) was connected to the h.p.l.c. equipment.

The g.f.a.a. system consisted of an atomic absorption spectrophotometer (Varian 475) equipped with a CRA-90 graphite furnace unit and an ASD-53 sample dispenser.

Standard solutions of sodium arsenite, disodium arsenate, dimethylarsinic acid (cacodylic acid) and MSMA were prepared by dissolving the compounds in glass-distilled, de-ionised water. Samples of four commercial MSMA formulations ('Farmers MSMA' from Farmers Organisation; 'Mesamate' from Farmers Organisation; 'Daconate' from Bayer and 'Target' from Pamol, Israel) were tested. The MSMA content of each of these water-soluble products was 720 g litre^{-1}, according to the manufacturers.

Elution solvents for the h.p.l.c. separation were water (solvent I) and a solution of reagent-grade 0·2-M ammonium carbonate in water (solvent II). All water was glass-distilled and de-ionised, and both solvents were filtered through Millipore filters (0·5 μm) before use.

A solution of nickel chloride in water (2000 μg Ni ml^{-1}) was prepared for use as matrix modifier for the g.f.a.a. determination of arsenic.

2.2 H.p.l.c. separation

Single standards were used to determine the retention time of each compound on the anion-exchange column. Thereafter a mixture of these standards was used to determine separation of a combination of arsenical compounds. The presence of arsenical compounds in MSMA formulations was investigated by chromatographing formulations on the h.p.l.c. column.

All volumes injected into the h.p.l.c. were 20-μl aliquots of dilutions which contained an expected arsenic concentration of 100 μg ml^{-1}. Samples of formulated MSMA were diluted as follows: 4·505 g of the formulation, supposed to contain 1 g of arsenic (720 g MSMA per 1500 g total mass contained in 1 litre formulation), was dissolved in water and the volume made up to 1 litre. Through further dilution (10 ml:100 ml water) the final concentration was obtained for injection into the h.p.l.c.

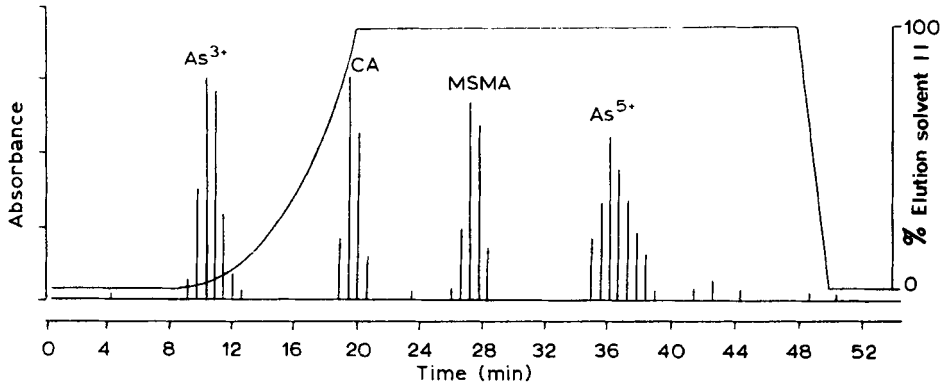

Fig. 1. Atomic absorption peaks of four arsenical compounds separated on an h.p.l.c. anion-exchange column: (As^{3+}) sodium arsenite; (CA) cacodylic acid; (As^{5+}) disodium arsenate.

A solvent programmer was used to create a concave flow profile from 100% solvent I (0% solvent II) to 100% solvent II (0% solvent I) during the time period 9–20 min after injection into the column, as shown in Fig. 1. The 100% level for solvent II was then maintained for 28 min before it was decreased to 0% (within 2 min), with a simultaneous increase to 100% of solvent I. The solvent flow rate through the anion-exchange column was 1·4 ml min^{-1} (pump pressure *ca.* 11 000 kPa).

Fractions (1 ml) of eluted solvent were collected on a fraction collector and analysed for arsenic by g.f.a.a.

For determination of total arsenic and MSMA, a dilution of each formulation containing an expected arsenic concentration of 0·30 μg ml^{-1} was injected into the g.f.a.a. without prior h.p.l.c. separation. The arsenic concentration thus found was converted to MSMA (g $litre^{-1}$) for comparison with the supposed MSMA concentration of 720 g $litre^{-1}$.

2.3 Analysis

An aliquot of 5 μl standard or sample solution was injected into the graphite tube. The heating cycle for the furnace comprised: drying at 100°C for 20 s, ashing at 900°C for 10 s, and atomising at 2400°C for a 3-s hold time. The ramp rate of temperature increase to atomising was 500°C s^{-1}. Peak height absorption measurements were made at the 193·7 nm arsenic line, using a hollow cathode lamp emitting at 7 mA. Deuterium lamp background correction was applied. The calibration curve technique was employed for quantification and a near-linear absorption range of between 0·10 and 0·50 μg ml^{-1} arsenic was obtained. The mean value of three determinations per sample was taken as the analytical result. The lowest detectable limit of arsenic was found to be approximately 0·25 ng. This corresponds to approximately 0·0017 g $litre^{-1}$ in the MSMA formulation samples.

Analysis of all samples and standards was immediately preceded by the addition of a matrix modifier, in the form of 10 μl nickel chloride solution (2000 μg Ni ml^{-1}), to the analyte.

3 RESULTS AND DISCUSSION

The arsenic absorbance peaks found in fractions of the mixture of eluted standards from the h.p.l.c., and the time in which they eluted, are presented in Fig. 1. The elution profile of the solvents is also shown in this figure. Adequate separation of the four compounds was achieved. Sodium arsenite eluted first, followed by cacodylic acid, then MSMA and finally disodium arsenate. As far as could be established, MSMA has not been included in previous studies on h.p.l.c. separation of arsenical compounds. By comparison, MSMA in Fig. 1 eluted at approximately the same position between cacodylic acid and arsenate as was found by Woolson[4] with methylarsonic acid under similar h.p.l.c. conditions.

Arsenic absorbance peaks from the h.p.l.c. fractions of two of the formulations ('Farmers MSMA' and 'Target'), are presented in Figs 2 and 3 respectively. The same elution profile was used as in Fig. 1. In contrast to the result regarding the mixture of standards (Fig. 1), peaks were only found in the fractions eluting at the retention time of MSMA in Figs 2 and 3. The same result applied to the fractions of 'Daconate' and 'Mesamate'.

Although arsenite and arsenate salts as well as cacodylic acid were not detected in any of the formulations examined, the possibility remained that another compound may have eluted at exactly the same time as MSMA. However, no excess of elemental arsenic could be detected in any of these formulations. The total arsenic content, expressed as a percentage of the expected concentration of the element were 98·0 in 'Farmers MSMA', 107·5 in 'Target', 103·8 in 'Daconate' and 96·3 in 'Mesamate'. Total MSMA, calculated according to the above percentages of elemental arsenic were 706, 774, 747 and 693 g litre^{-1} for 'Farmers MSMA', 'Target', 'Daconate' and 'Mesamate', respectively. Although the formulations' total MSMA contents were not all within the limits of 702–738 g litre^{-1} as required according to local Regulation R2561 of 1982 (Act 36 of 1947), none of them contained MSMA at excessive levels. Even the 774 g litre^{-1} found in the 'Target' formulation was only about 5% in excess of the required limit of 738 g litre^{-1}. The acute oral LD_{50} of MSMA for rats is as high as 900 mg kg^{-1}.[6]

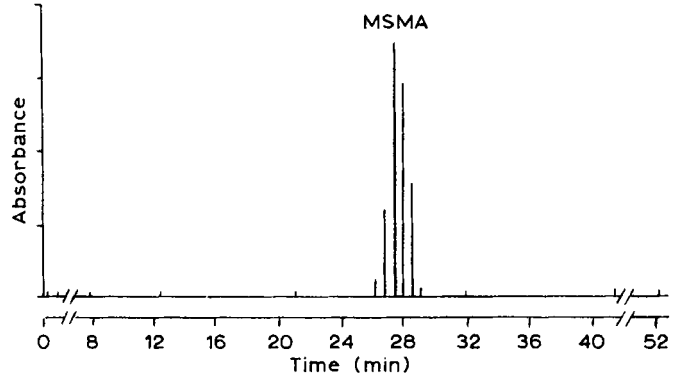

Fig. 2. H.p.l.c.–g.f.a.a. chromatogram of 'Farmers MSMA' formulation.

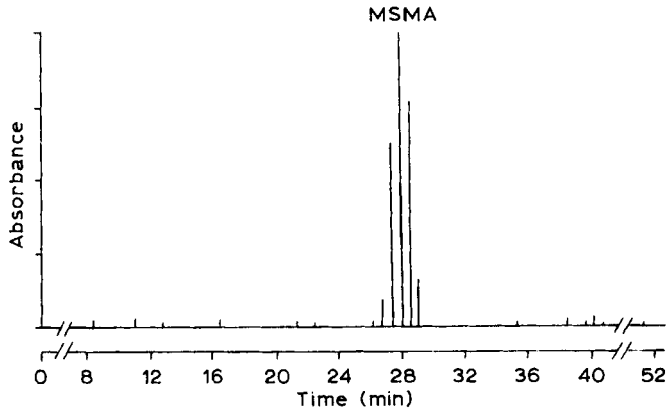

Fig. 3. H.p.l.c.–g.f.a.a. chromatogram of 'Target' formulated MSMA.

Therefore it seems unlikely that a 5% increase in active ingredient of a MSMA formulation would be sufficient to cause animal toxicity.

From these studies it appeared that all the formulations tested contained only MSMA at concentrations close to the supposed level. It also seems reasonable to conclude that for routine quality control analysis of MSMA formulations, determination of total arsenic alone should be sufficient. However, analysis for contaminants should be done on each batch used for spraying extensive grazing farms, so as to preclude the possibility of wholesale intoxication of grazing animals.

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