Rapid Screening Method for the Analysis of Paraquat and Diquat by LC/MSD Using Selective Ion Monitoring and Large Volume Injection

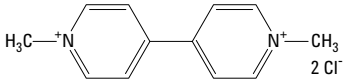
Application

Environmental

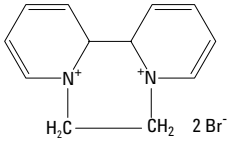
Author

Neil Cullum
Anglian Water Laboratories
Huntingdon, UK

Paul Stephens
Agilent Technologies, Ltd.
Bracknell, UK



Paraquat



Diquat

Abstract

A rapid and sensitive method for the analysis of paraquat and diquat was developed using LC/MS, electrospray ionisation (ESI), positive ion mode, selective ion monitoring (SIM) large volume injections, and minimal sample preparation. No trace enrichment was required to obtain limits of detection (LOD) below 1 µg/L, which is well below the World Health Organisation (WHO) advisory value of 10 µg/L.

Introduction

Paraquat and diquat, bipyridilium salts, are used in agriculture as non-selective contact herbicides. They are also commonly used in commercial weed killer formulations for domestic weed control.

Standard analytical methods for these herbicides in water matrices involve solid phase extraction as the enrichment technique and analysis by liquid chromatography using diode array detection (DAD) [1]. The LOD for paraquat and diquat is reported to be less than 0.4 µg/L.

This application note gives details for the screening of these herbicides using liquid chromatography/ mass spectrometry (LC/MS) and a direct aqueous injection of the sample, thereby eliminating the trace enrichment step.

The WHO has set an advisory value of 10 µg/L for paraquat in drinking water. In this application, a LOD of well below 1 µg/L is achieved for paraquat and diquat, as well as for amitrole and chlormequat.

The method presented uses an ion-pairing reagent to help separate the compounds and to prepare

the analyte as an ion. Typical ion-pairing reagents such as hexanesulphonic acid are non-volatile and cause the ion-pair complex to become non-volatile. The ion-pair reagent used in this application is tridecafluoroheptanoic acid (TDFHA), which has been reported as suitable for the analysis of basic pesticides and sufficiently volatile for the electrospray interface [2].

Experimental

All analyses were performed using Agilent 1100 series LC/MSD quadrupole coupled to an Agilent 1100 series LC system consisting of a quaternary pump, autosampler, thermostated column compartment, vacuum degasser and diode array detector. The quadrupole mass spectrometer was operated with an atmospheric pressure electrospray ionisation (API-ES) source in positive ion mode.

HPLC conditions

Column:	Zorbax Extend C18, 150 mm long × 2.1 mm id, 3.5 µm particles, 60 °C
Flow rate:	0.4 mL/min
Injection volume:	250 µL
Mobile phase:	Isocratic elution A: 5 mM TDFHA in water (75%) B: Acetonitrile (ACN) (25%)

MS conditions

Ionisation mode:	API-ES, Positive
Drying gas flow:	13.0 L/min
Nebulizer gas pressure:	30 psig
Drying gas temperature:	350 °C
V_{cap} voltage:	3500 V

The SIM ions and fragmentor voltages listed in the SIM table parameters were all optimised using Flow Injection Analysis (FIA). Ten mg/L standard solutions of each herbicide were prepared in 5 mM TDFHA and injected using scan mode 50 to 1000 amu. The fragmentor voltage was ramped from 50 to 200 V in 10 V steps. The fragmentor voltage generating the maximum response for each SIM ion was selected.

Table 1. SIM Table Parameters

Compound	Time	Group	SIM ion	Frag volt	Gain	Res
Amitrole	0	1	85.1	120	1.0	Low
Chlormequat			122.0	130		
Diquat			183.0	140		
Paraquat			185.0	140		

Mass spectra for diquat and paraquat appear in Figures 1 and 2 respectively.

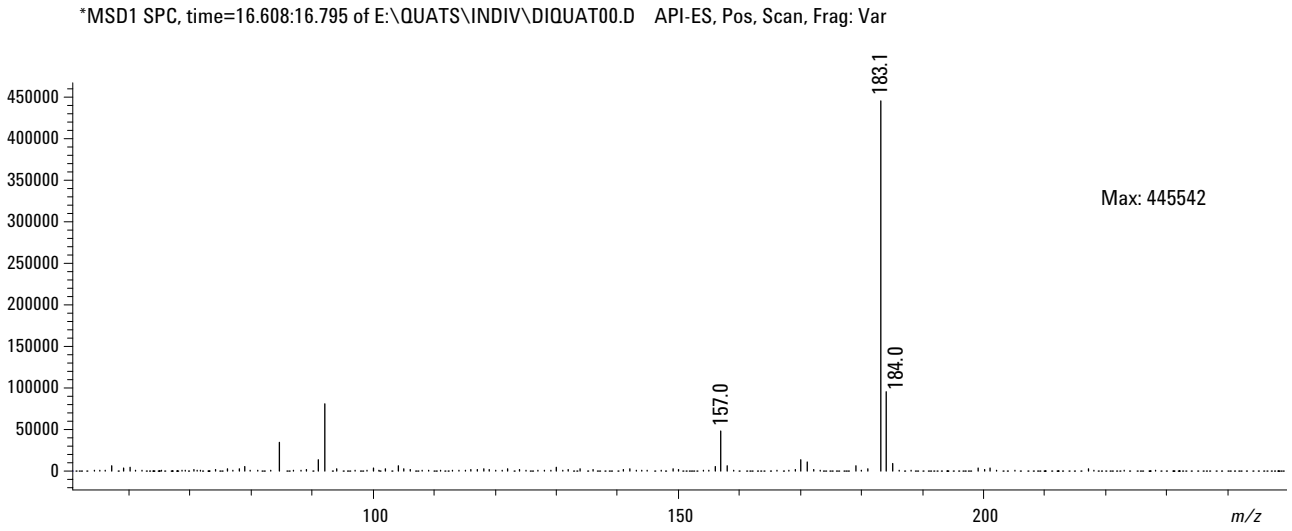


Figure 1. Mass spectrum of diquat.

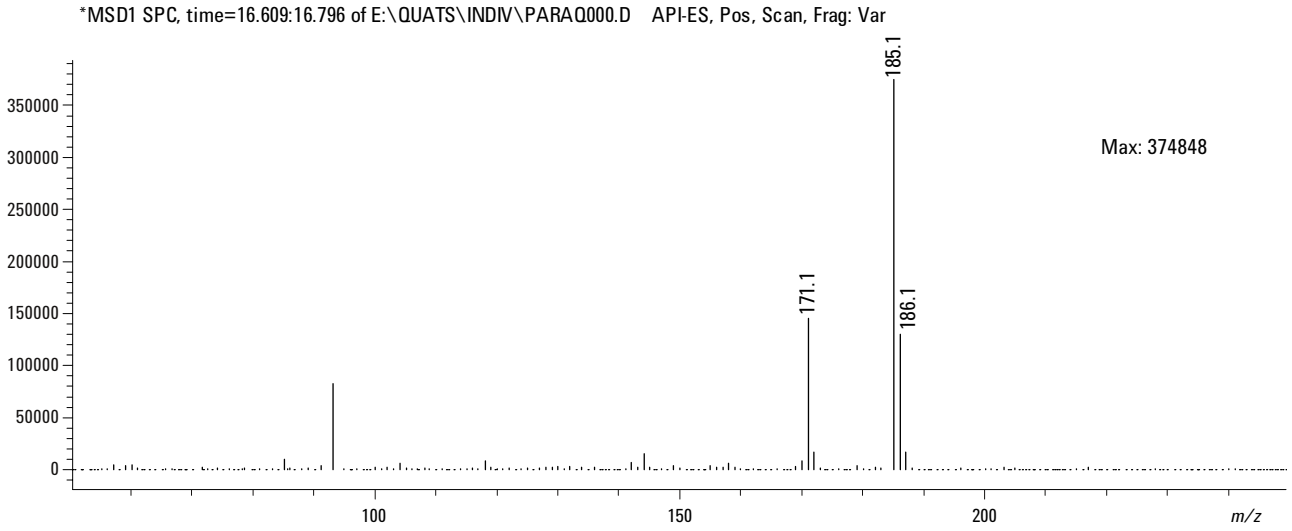


Figure 2. Mass spectrum of paraquat.

Sample Preparation

The only preparation required is that both working calibration standards and samples contain TDFHA at a concentration of 5 mM.

Figure 3 shows a typical chromatogram for a 10 µg/L calibration standard.

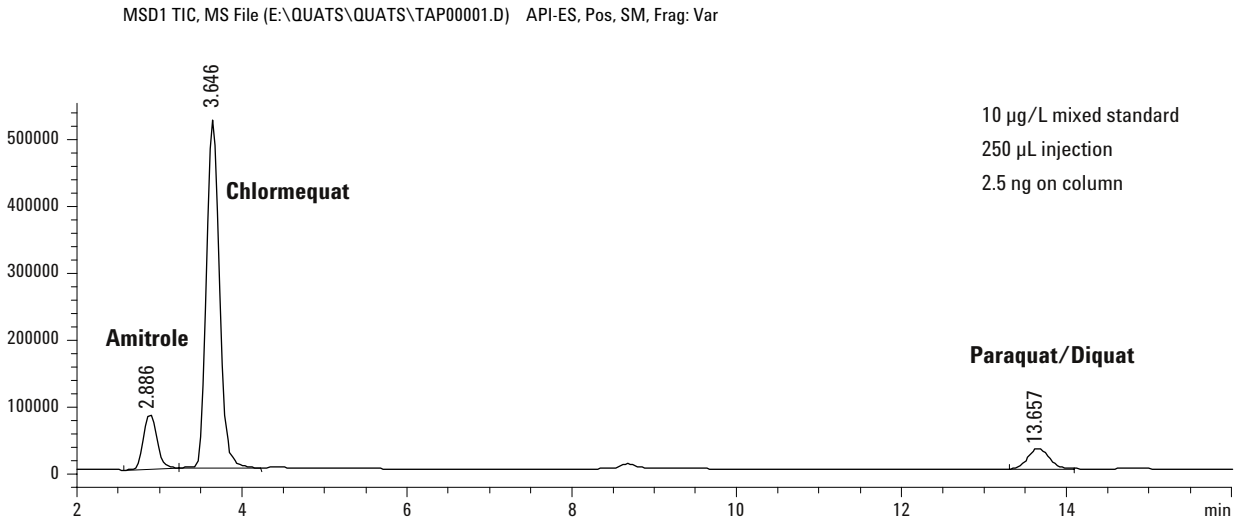


Figure 3. Total ion chromatogram of mixed standard, 10 µg/L, 250 µL injection, 2.5 ng on column.

Figures 4 and 5 show extracted ion chromatograms for diquat and paraquat, respectively, spiked into borehole water at a concentration of 1 µg/L.

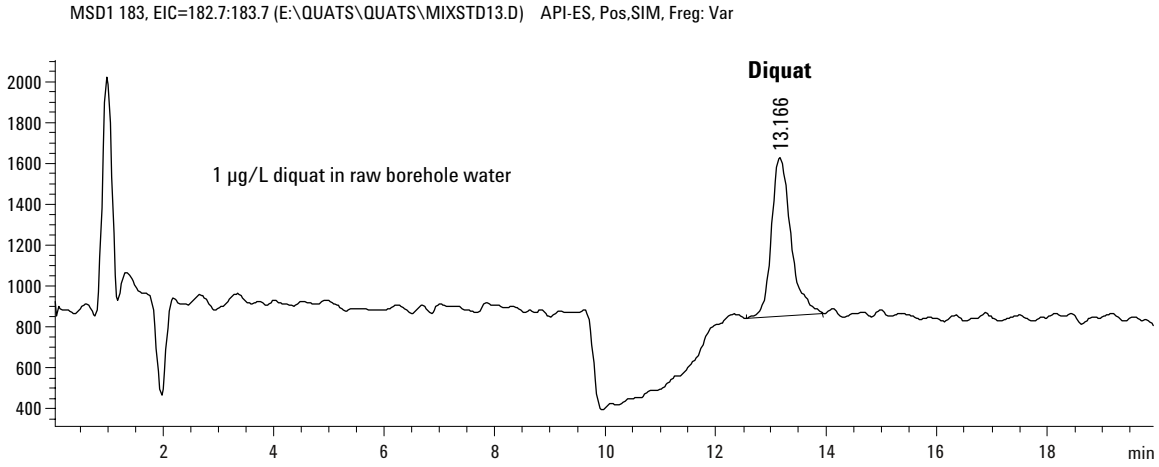


Figure 4. Extracted ion chromatogram of 1 µg/L diquat in raw borehole water.

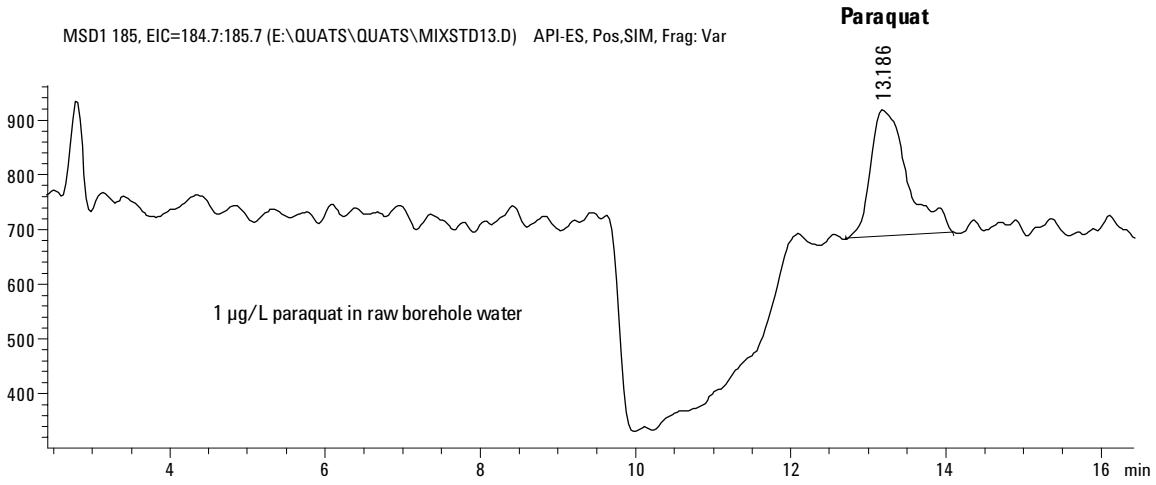


Figure 5. Extracted ion chromatogram of 1 µg/L paraquat in raw borehole water.

Conclusion

The data shows that the method presented is capable of screening for the four herbicides with a run time of 20 minutes per sample. No trace enrichment is required to obtain limits of detection below 1 µg/L with minimal sample preparation.

References

1. Analysis of Paraquat and Diquat by HPLC. Agilent publication number 5966-1875E, 1997.
2. Impact of Ion-pair Reagents on LC/MS Analysis. Agilent publication number 5968-8659E, 2000.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
August 7, 2002
5988-7220EN

Agilent Technologies