

A SENSITIVE UPLC-MS/MS METHOD FOR DETERMINATION OF THE ACQ WOOD PRESERVATIVE QUAT IN ENVIRONMENTAL WATERS

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INTRODUCTION

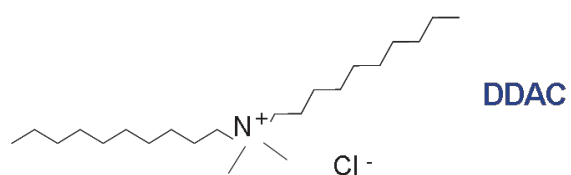
Wooden utility poles must be treated with preservatives to protect against insects, fungi, and other environmental damage. A number of different preservatives have been employed for this purpose such as pentachlorophenol, coal tar creosote and copper chromium arsenic, but the toxicity of these substances is of environmental concern. The Electric Power Research Institute (EPRI) is investigating the effectiveness of commercially available prevention methods to reduce preservative migration from treated wood poles and to compare the migration of constituents of various wood treatments.

Ammoniacal copper quat (ACQ) is one of the treatment chemicals being studied. ACQ combines copper oxide with the quaternary ammonium ion DDA⁺ (didecyltrimethylammonium). Over the past eight years a number of wooden poles, treated with ACQ, were installed at a study site in Florida. Each pole was planted above a custom made lysimeter designed to gather rainwater that contacts the poles and percolates through the ground. Periodically, water was collected from the lysimeters to be analyzed for DDA⁺ (reported as the chloride salt DDAC).

The concentrations of DDA⁺ in the captured rainwater were very low. Currently, there is no official method for the determination of DDA⁺ at low ppb or sub-ppb concentrations in water samples.

A highly sensitive and selective method was developed for determination of DDA⁺ in the water samples taken from the lysimeters. Solid-phase extraction (SPE) was performed using Oasis WCX, a mixed-mode weak cation-exchange SPE sorbent. After SPE, the isolated DDA⁺ was quantified using UPLC/MS(MS). Detection limits well below 1 µg/L (ppb) were demonstrated for groundwater or surface water.

The composition of ACQ is 66.7% CuO and 33.3% didecyltrimethylammonium chloride.



DDAC has surfactant and complexing activity; CuO is a biocide

Study Design

A number of posts treated with ACQ were planted in the ground above a custom made lysimeter designed to gather all the rainwater that contacts the posts and percolates through the ground.



A one inch diameter monitoring well was installed in each lysimeter to facilitate sampling of the accumulated rainwater. Periodically, as the lysimeters fill, the water is collected and sent to the laboratory for analysis.

METHOD DEVELOPMENT

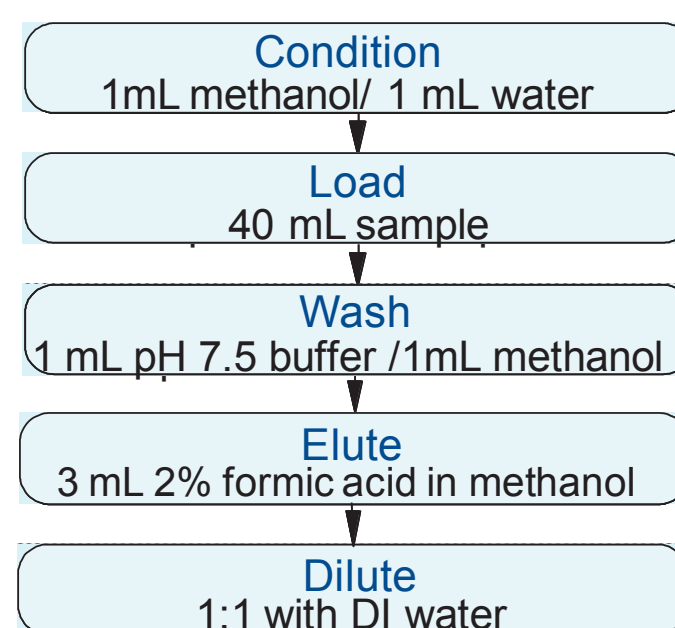
An Analytical Method was Developed with the Following Objectives

- Simple extraction of DDAC with relatively low volumes of sample
- Minimal sample cleanup
- LC separation from other polar compounds in natural water samples
- Reliable identification of DDAC
- Detection limits approaching 0.01 ppb
- Method precision and accuracy suitable for environmental studies

SAMPLE PREPARATION

Samples were collected in pre-cleaned glass bottles with Teflon lined caps. The samples were kept at 4 °C prior to SPE analysis.

Oasis WCX Cartridge SPE 3cc, 60 mg



LC-MS/MS

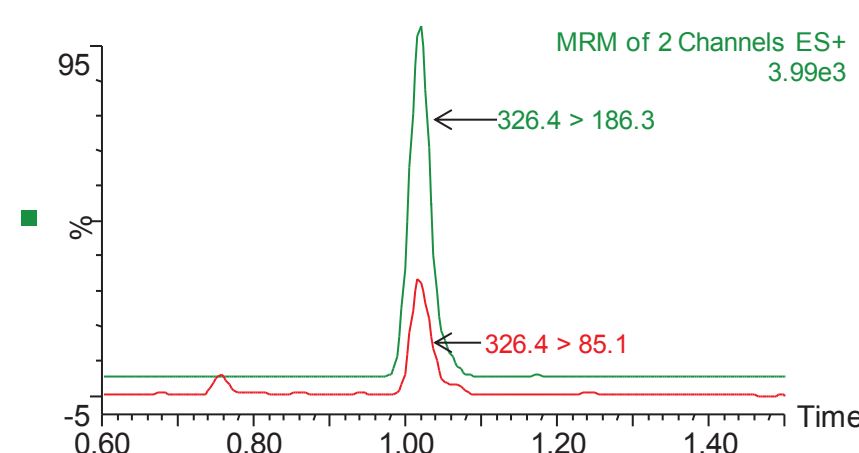
LC Parameters Waters ACQUITY H-Class UPLC

Column: ACQUITY HSS C₁₈ 2.1x50 mm x 1.7 µm
 Mobile Phase : Isocratic @ 80:20 A/B
 A: acetonitrile
 B: 40 mM ammonium formate in water (pH 3.7)
 Flowrate: 0.50 mL/min
 Injection: 10 µL
 Temperature: 35 °C

Waters ACQUITY TQD Mass Spectrometer

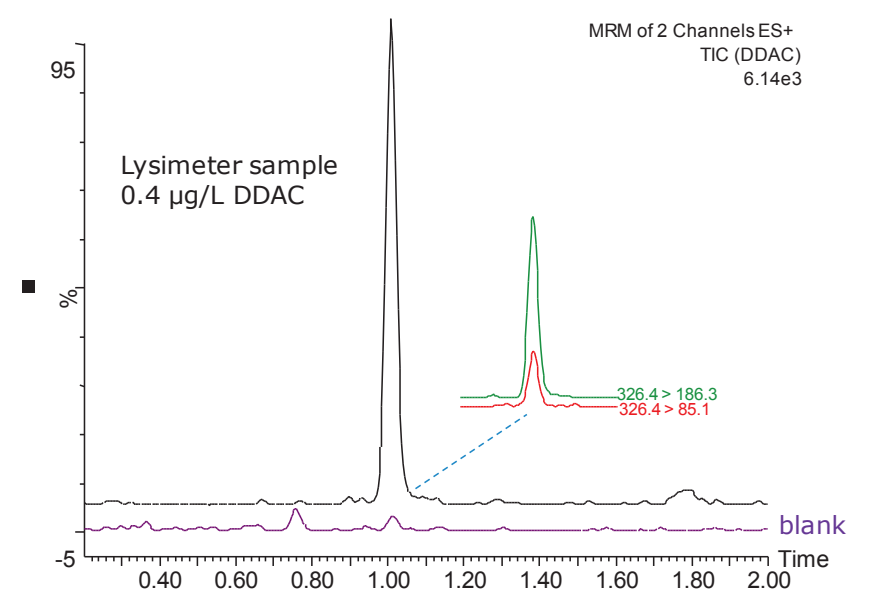
Electrospray positive mode (ESI+)
 MRM transitions: 1) m/z 326.4>186.3
 2) m/z 326.4>85.1
 Cone voltage: 30 V
 Collision cell energies: 25 eV (MRM 1)
 30 eV (MRM 2)

Calibration was linear ($r^2 = 0.998$) for six point curve from 0.02 to 50 ng/mL. A typical UPLC-MS calibration standard (0.3 µg/L) is shown below showing the relative response for each MRM transition.



RESULTS LC-MS/MS

Shown below is a UPLC-MS/MS chromatogram obtained from analysis of a collected rainwater sample. The insert shows the ion ratio for the two MRMs.



DDAC was detected at low concentrations in the lysimeter samples, from 0.02 to 0.4 µg/L.

No DDAC was detected in any method blank above 0.005 µg/L.

DISCUSSION

DDAC has been determined by a number of chromatographic techniques including HPLC with evaporative light-scattering detection (HPLC-ELSD)¹ and with ion-chromatography². Because these methodologies are not sufficiently sensitive or selective for the EPRI study an LC-MS based method was developed. For the first round of samples HPLC-MS with a single quadrupole instrument was employed for the analysis. Later the method was upgraded to tandem mass-spectrometry with improvement in selectivity³. Ultimately, the UPLC-MS/MS method presented in this poster was developed with even better sensitivity and selectivity as well as a threefold decrease in analysis time. The LOQ for the current method is 0.01 µg/L (10 ppt).

Oasis WCX is a mixed-mode weak cation-exchange sorbent, highly suitable for determination of DDAC and other quaternary ammonium compounds in aqueous samples. For example, chlormequat and mepiquat have been determined using this sorbent³. Also, paraquat and diquat have been determined in drinking water using Oasis WCX cartridges (see NACRW poster 66)⁴.

CONCLUSIONS

- DDAC was quantitatively recovered from collected rain water using the Oasis WCX SPE cartridge
- A UPLC-MS/MS method was demonstrated with LOQ of 0.01 µg/L (ppb) using a 40 mL sample
- DDAC was clearly identified and quantified by LC-MS/MS in captured rainwater
- The Oasis WCX cartridge is effective for other "Quats"

References

1. C. Daniels, J. Chromatog. Sci., **30**, pp 497-499, 1992
2. G. Vincent et. al., Environ. Monitor. Assess., **133**, pp 25-30, 2007
3. D. Mauro and M. Young, Pittcon paper 910-8, 2006
4. D. Mauro and M. Young, NACRW poster 66, 2013