

AUTOMATED METHOD FOR THE EXTRACTION AND DERIVATISATION OF ALKYLPHENOLS, ETHOXYLATES AND BISPHEENOL A IN WATER

Jonathan Dunscombe, Phine Banks, Anatune Ltd, Cambridge, UK, John Quick, ALS, Coventry, UK.

INTRODUCTION

For most applications and industries, employing automation brings the advantages of consistency and reproducibility, increased throughput and a reduction in the risks associated with sample preparation. For environmental testing methods especially, automation has demonstrated the capability to deal with a range of methodologies and this has been demonstrated in earlier works published by Anatune in collaboration with customers.

Environmental testing also calls for the analysis of many compound types, alkylphenols and alkylphenol ethoxylates being one such group. These compounds can pose a particular hazard to the health of humans and wildlife possessing classification of endocrine disruptors, more specifically, xenoestrogens, a chemicals class which have the ability to mimic oestrogen in the body. This comes from the similarity in chemical structure between the alkylphenols and oestrogen.

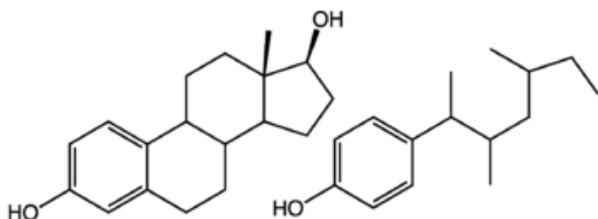


Figure 1. Chemical structure of oestrogen (left) and a nonylphenol (right).

This application note describes a fully automated method for the extraction and derivatisation of alkylphenols, their ethoxylates and bisphenol A as developed by John Quick at ALS, Coventry with analysis using an Agilent 7000C triple quadrupole mass spectrometer in negative chemical ionisation (NCI). Using pentafluorobenzoyl chloride as the derivatisation reagent both improves chromatographic performance and also increases sensitivity and amenability to be ionised by NCI. The developed method acquired accreditation for four compounds in this suite: 4-n-nonylphenol, 4-nonylphenol (technical) 4-tert-octylphenol and bisphenol A with a full eleven batch validation performed on each of these compounds in a range of matrices.

INSTRUMENTATION

Autosampler:

Dual head MPS XT

GERSTEL mVorex

GERSTEL Solvent Filling Station

Anatune CF200 Centrifuge

GC-MS:

Agilent GC 7890B – 7000C triple quadrupole in negative CI mode.



Figure 2. GERSTEL Dual Head MPS XT at ALS Coventry

METHOD

To 500 mL of sample, 5 mL of 5M sodium hydroxide was added and the sample inverted. From this, 5 mL of sample was manually pipetted into a 10 mL vial followed by a further aliquot of sodium hydroxide (5M), and 0.5 mL of methanol. The remainder of the process was then automated. All calibration, AQC and internal standard spiking was carried out by the MPS. 2.5 mL of hexane containing 0.1% pentafluorobenzoyl chloride (PFBCI). The sample was then mixed in the vortexer for three minutes. An aliquot of IPA was added to aid in breaking any formed emulsions, followed by centrifugation for three minutes. A portion of this extract was transferred to a GC autosampler vial ready for analysis. The samples are injected using a 40 µL large volume injection.

RESULTS

Table 1 contains the Limit of Detection (LODs) for the suite of ten compounds in this method. These values and subsequent values for precision and bias have been calculated from an NS30 validation.

Table 1. Compounds and their calculated LODs

Det Name	CAS	LOD (µg/L)
4-tert-Octylphenol	140-66-9	0.00312
4-n-Nonylphenol	104-40-5	0.0966
Bisphenol A	80-05-7	0.0389
4-Nonylphenol (technical)	84852-15-3	0.00457
4-Octylphenol Monoethoxylate	2315-67-5	0.00748
4-Octylphenol Diethoxylate	2315-61-9	0.0106
4-Octylphenol Triethoxylate	2315-62-0	0.0203
4-Nonylphenol Monoethoxylate	104-35-8	0.0348
4-Nonylphenol Diethoxylate	20427-84-3	0.0424
4-Nonylphenol Triethoxylate	51437-95-7	0.0413

Figure 3 displays a chromatogram for 4-tert-Octylphenol in sewage effluent at a level of 0.01 µg/L compared to a blank extract.

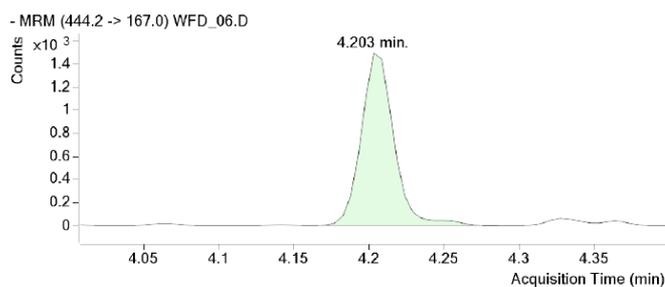


Figure 3. Chromatogram at 0.01 µg/L, 4-tert-octylphenol monoethoxylate

To validate and assess the performance of the method, a full eleven batch validation was carried out with a maximum of two batches per day with samples spiked at 20% and 80% of the calibration range. Four compounds were fully accredited; 4-tert-octylphenol, 4-n-nonylphenol, 4-nonylphenol (technical) and bisphenol A. Relative Standard Deviations (RSDs) were between 3 to 14% with 15% being the upper accepted limit. Figure 4 shows the recoveries for these four compounds in four water types – Blank laboratory, surface, ground and saline waters at 20% and 80% of their respective calibration ranges. Correlation coefficients of 0.995 or greater were achieved for all analytes. Figure 5 shows the calibration curves for 4-nonylphenol-triethoxylate and 4-octylphenol-monoethoxylate.

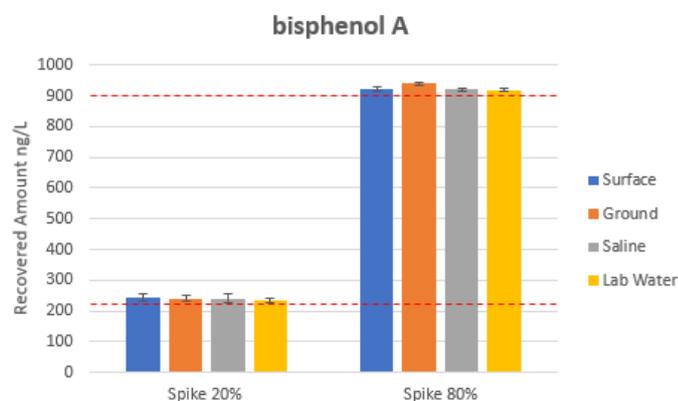
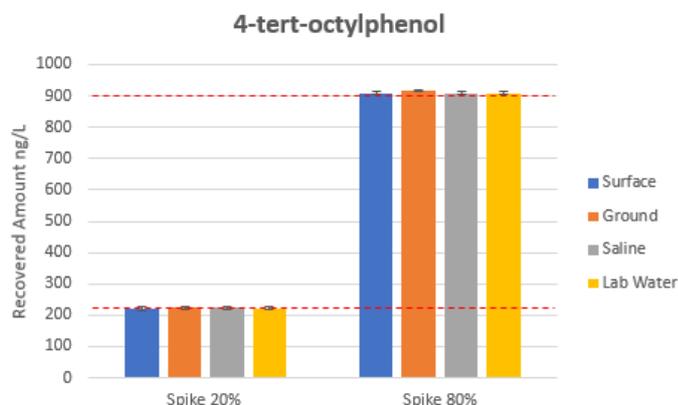
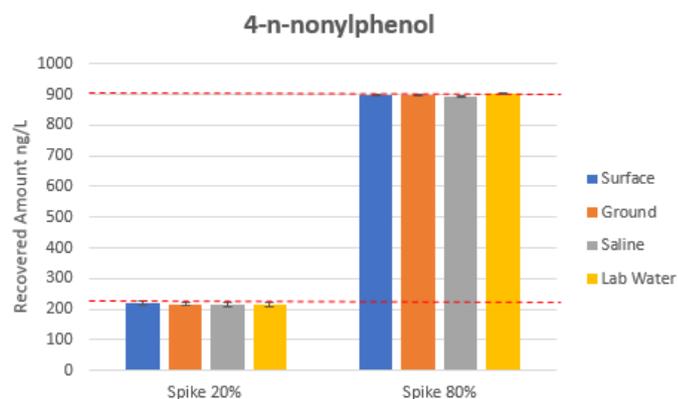
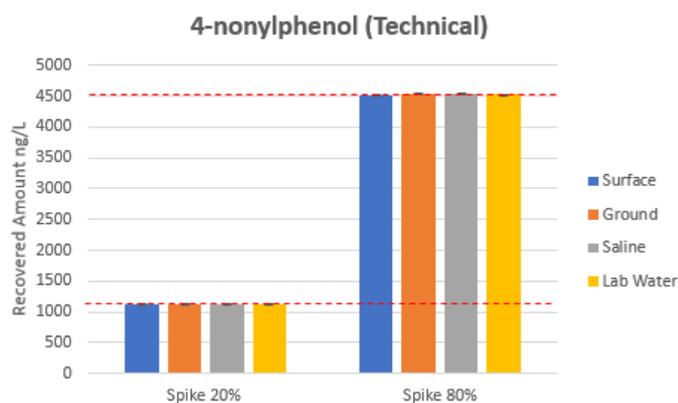


Figure 1: Recoveries of four tested analytes at 20% and 80% of the calibration ranges in each of the four matrices: Blank laboratory, surface, ground and saline water.

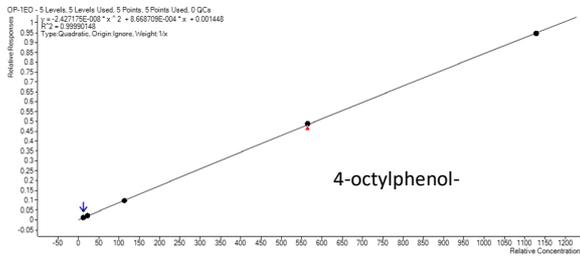
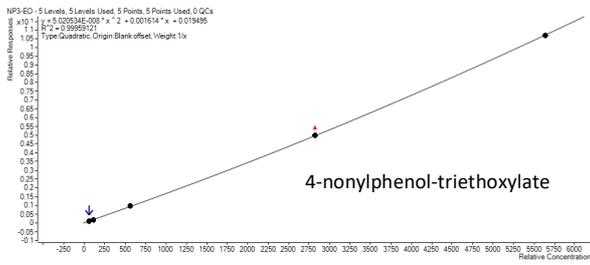


Figure 5: Calibration curves for 4-nonylphenol-triethoxylate and 4-octylphenol-monoethoxylate. $R^2 \geq 0.995$.

CONCLUSIONS

This application note demonstrates the fully automated extraction and derivatization of alkylphenols and their ethoxylate derivatives with precision and bias falling within their regulatory limits required. Good correlation coefficients were obtained for all analytes. Full accreditation was obtained for four analytes with validation in a range of matrices demonstrating the ability of the method and also of the automation to deal with a variation of sample types and matrix effects.