

Offline Sample preparation of Acid Herbicide Samples for LC/MS analysis using a dual head MultiPurpose Sampler

Sean O'Connor, Anatune Ltd. Girton, Cambridgeshire (UK).

Introduction

Throughout the water industry, the need for quick reliable sample preparation and testing is required to determine a wide range of analytes. In conjunction with James Kee at Thames Water, Anatune helped design a system (Based upon the GERSTEL MultiPurpose Sampler and associated hardware) which would enable the offline sample preparation for acid herbicide, non-polar pesticides and metaldehyde analysis. This application note focuses on the sample preparation for acid herbicide analysis and the results obtained. These results are compared with results obtained by manual preparation.

Instrumentation

GERSTEL MultiPurpose Sampler (MPS) 2 XL-xt Dual Head configuration
 Left Head configured with 1 mL Liquid Syringe
 Right Head configured with 10 µL Liquid Syringe
 GERSTEL Agitator
 GERSTEL Maestro software integrated



Method

Original manual method : Samples were collected in 1 L bottles and 250 mL of the sample was transferred to flask with sodium thiosulphate to remove chlorine. A 1 mL aliquot of formic acid, to reduce the pH, and internal standard solution were added to the flask, mixed well and an aliquot was transferred to a 2 mL HPLC vial for analysis.

Automated method : Samples were collected in 40 mL vial with sodium thiosulphate to remove chlorine. All further steps were automated. A 1 mL aliquot of the sample was transferred from the collection vial to a 2 mL HPLC vial using the 1 mL liquid syringe installed in the left hand side MPS Head. This was rinsed with clean water between samples. An internal standard solution and a formic acid solution was added with the right hand side MPS Head which had a 10 µL syringe installed. Although the agitator was available it was not required as the solutions were homogeneous without mixing as the volumes were small.

Sample analysis: The prepared samples were analysed using online solid phase extraction and liquid chromatography with a triple quadrupole mass spectrometer (LC/QQQ).

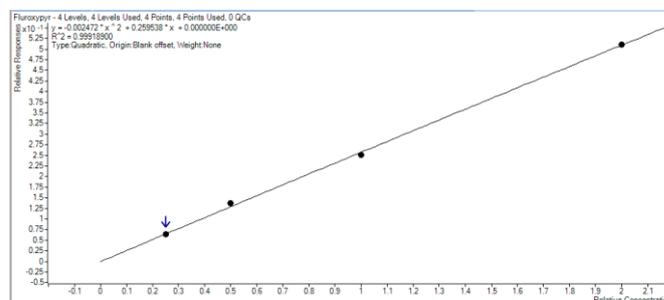
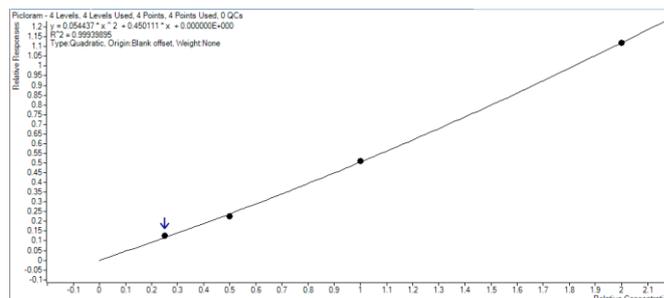
Results

The analytes determined in this method were as shown in Table 1

Table 1: Analytes determined

Clopyralid	Picloram	Dicamba
Bromoxynil	2,4-D	2,4,5-T
Triclopyr	Fenoprop	Dichlorprop
MCPB	MCPP (Mecoprop)	Fluroxypyr
Pentachlorophenol	2,4-DB	Bentazone
Ioxynil	MCPA	

The results obtained using the MPS showed good correlation with standard concentration when prepared as described in the method for each of the acid herbicides analysed.



To measure the reproducibility of the preparation of both the manual and automated method, the peak area of the three internal standards over 42 analytical runs (a typical number of samples per batch) was averaged and a percent residual square deviation (%RSD) was calculated and the results are



shown in Table 2.

Table 2: Calculated %RSD of peak areas of internal standards (n=42)

%RSD	Manual	Automated
¹³ C ₆ -2,4-D	3.96	3.89
¹³ C ₆ -Dichloroprop	4.41	3.64
¹³ C ₆ -PCP	6.22	5.50

The time taken to prepare the 42 samples manually was between 3 and 4 hours of analyst time. Utilising the GERSTEL Automated approach, analyst time was reduced nearly completely. The time taken to prepare the 42 samples with the GERSTEL MultiPurpose Sampler was approximately 1 ½ hours.

Discussion

This applications note shows that by automating a simple, yet time-consuming protocol, savings can be made but not at the detriment of sample results and system performance. A number of indirect advantages are obtained which come from a knock-on effect from a change to the workflow, and these are explained below.

Automation using the GERSTEL MPS2 delivers the same level of reproducibility whenever it is used because human error is eliminated from the process. This will reduce the need to repeat sample analysis due to any errors in manual preparation which will increase sample throughput and overall cost of analysis.

A reduction in sample preparation time allows samples to be analysed more quickly, thereby reducing result turnaround time. More samples are also able to be prepared in the same time frame as a manual preparation, so if sample numbers increase, they will not impact on analyst daily workloads.

As this automated approach requires little or no user intervention, analysts and technicians can be redeployed onto other laboratory activities whilst the samples are prepared automatically.

The sample size and volumes of reagents were reduced considerably from the manual method with reductions in the order of 25 times. This both reduces the cost of acquiring expensive solvents and reagents and also reduces the volumes being handled by laboratory staff, making the preparation safer.

Smaller sample sizes present further advantages to Water Utilities companies. A smaller sample vessel can reduce its cost per sample, along with being able to be transported more cheaply due to it weighing less. Sampler Technicians are able to be more productive by filling up with less water per household, and fit more samples into the sample vehicles per day.

Storage of samples once at the laboratory is also improved as the smaller sample sizes will take up less fridge space.

Automation of the sample preparation also comes with the added benefit of being able to be performed during times when the laboratory is closed, as samples can be prepared, unattended and accurately, ready for analysis when the laboratory reopens.

The overall conclusion from this work would be that the GERSTEL MPS 2 can provide quick, reproducible sample preparation, enabling cost reductions

in analysis and freeing up laboratory staff time. An improvement in the workflow allows for more time to develop new methods, gives staff the chance to participate in training and professional development and also grow the business.

Acknowledgements

We would like to thank James Kee of Thames Water Utilities (Reading) for completing the practical work and providing the data for this application note and Jeff Stubbs, Anatune - Water Analysis Specialist, for his contribution to the writing of this application note.