THE TOTAL DIGESTION OF MARINE SEDIMENTS USING AN AUTOMATED MICROWAVE DIGESTION TECHNIQUE FOR THE ANALYSIS OF TRACE METALS

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Introduction

To prepare sediments samples for introduction to most analytical instruments requires the sample to be dissolved in a liquid, in the case of a total decomposition of a marine sediment the use of hydrofluoric acid is required to bring the metals associated with the silica matrix into solution. This laboratory had from 1990 till recently used conventional closed vessel microwave 'bombs' with microwave heating to digest marine sediments. This method was particularly time consuming in terms of staff time and involved handling the hydrofluoric acid several times. To minimise the handling of hydrofluoric acid and keep the sample enclosed throughout the decomposition, an automated microwave digestion unit, QPrep5000 was evaluated for use. This microwave system is able to digest samples individually with full automation, thereby reducing staff time considerably; this also allows the temperature of each sample to be monitored.

Why Do We Digest
Most analytical instruments require the sample to be presented in a solution.
By dissolving the sample in a liquid, a homogenous mixture is produced.
The sample can be selectively extracted.
All species of one element present can be converted to one uniform form.
Calibration standards can easily be produced.
Sample can be easily spiked for internal standards, recovery or isotope dilution.

Table 1

Method

Tables 1 and 2 describe why we need to digest and problems, which can occur in doing so. Table 3 gives an overview of the method utilising closed vessels. In this case the CEM 2000 microwave, figure 1, this unit takes 12 vessels. The main problem with this method is that it is time consuming, as the vessels have to be opened for addition of boric acid, this also increases risk of contact with hydrofluoric acid. Table 4 gives an overview of the new method utilising the QPREP 5000 automated microwave digestion system. This allows unattended operation of up to 60 samples. As the sample is returned to boric acid while slightly hot there is little need for re-heating, if this is required it can be accomplished by using the in-situ water-bath. The contact with hydrofluoric acid is minimal thereby reducing risk to the operator. Figure 2 shows a flow diagram of the QPREP.

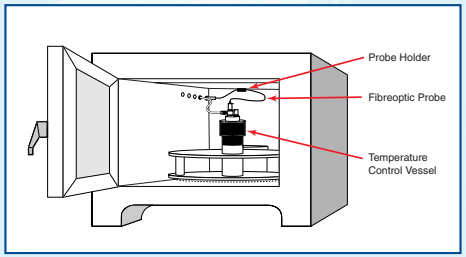

Figure 1

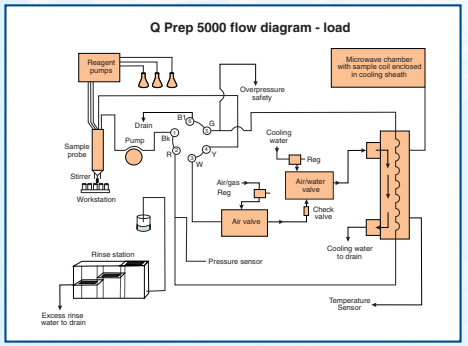

Figure 2

Sources of Error During Digestion	
Incomplete mineralisation	May be a requirement
Contamination vessels	From air, reagents or sample vessels
Volatilisation	Certain elements may be lost As, Hg, Se
Spray	From the reaction vessel
Adsorption	Onto sides of reaction vessel

Table 2

Total Digestion Method
1. 0.2-0.5G SAMPLE
2. 3 MLS HYDROFLUORIC ACID
3. 1ML NITRIC ACID
4. CLOSE VESSEL
5. CEM 2000 MICROWAVE DIGESTION SYSTEM
6. 165-175°C FOR ONE HOUR
7. COOL. OPEN VESSEL AND ADD BORIC ACID
8. CLOSE VESSEL AND REHEAT FOR 30 MINUTES AT 100°C

Table 3

Total Digestion - QPREP Method
1. WEIGH UP TO 0.5G SAMPLE
2. PLACE IN AUTOSAMPLER, UP TO 60 MAY BE ADDED
3. SYSTEM ADDS REAGENTS, 6ML HF AND 3 ML NITRIC
4. PLACE RECEIVER CONTAINER IN AUTOSAMPLER WITH 5.6G BORIC ACID
5. SET AUTOSAMPLER TO RUN
6. HAVE A CUP OF TEA
7. RETURN TO COMPLETED DIGESTS

Table 4

Results

A series of different weights of sample against digestion time at 190°C were run to establish minimum time required to complete digestion. Analysis of Al was made by atomic absorption spectrometry, all other elements were analysed by inductively coupled plasma mass spectrometry. In figure 3, analysis of lead, complete digestion is achieved after about 300 seconds, with little difference due to weight. Figure 4, aluminium, again this shows complete digestion after 300 seconds but with more variability particularly with the 0.5g samples. This might however be due to problems associated with aluminium fluoride precipitation after digestion. Figure 5, zinc, shows that although there is little difference for weight taken at least 600 seconds are required to complete digestion. Table 5 shows the recoveries achieved from a 10 ppb spike into a blank. Results indicate that the system is capable of producing a full digest with recoveries of metals, Li, Al, Mn, Ni, Zn, Rb, Cd, and Pb in the range of 97-110%.

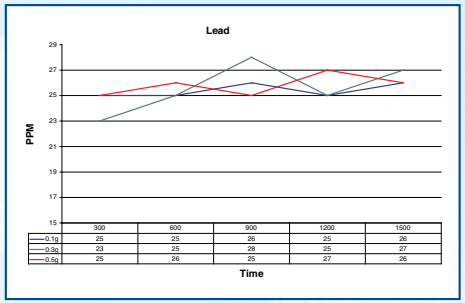

Figure 3

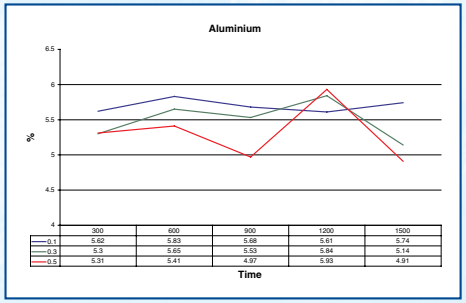

Figure 4

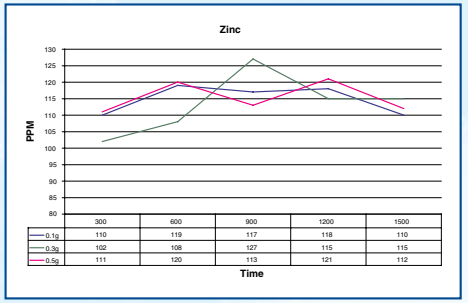

Figure 5

Recoveries from 10 ppb spike	
Lithium	97%
Aluminium	102%
Chromium	117%
Manganese	110%
Nickel	104%
Zinc	102%
Rhubidium	100%
Cadmium	102%
Lead	109%

Table 5

Comparison of three reference materials						
	PACS-1 Harbour sediment		MESS-2 Esturine sediment		BCSS-1 Esturine sediment	
Elements	Target	Mean	Target	Mean	Target	Mean
Arsenic			20.7	18	11.1	9.9
Cadmium	2.38	2.27	0.24	0.3	0.25	0.32
Chromium	113	98	106	98	123	99
Copper	452	417	39.3	36	18.5	17.2
Manganese	470	450	365	340	229	217
Nickel	44.1	46	49.3	53	55	54
Lead	404	432	21.9	24	28	24
Zinc	824	808	172	155	119	109

Table 6

Conclusions

A comparison of results achieved by this method for three certified reference materials is given in table 6. Which shows that while this automated method frees up operator time, it is capable of producing a complete digest of marine sediments suitable for marine monitoring purposes.

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