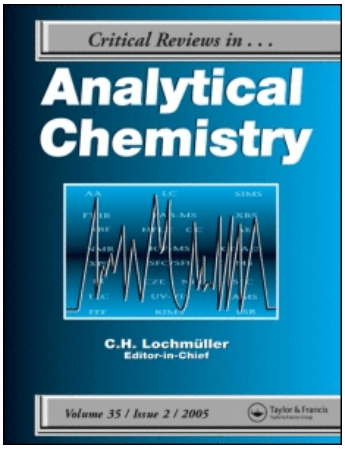

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DETERMINATION OF TRACE METALS IN BIOLOGICAL SAMPLES BY ATOMIC EMISSION AND ABSORPTION. MICROWAVE-ASSISTED SAMPLE PREPARATION

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Introduction

The use of microwave systems to oxidize the organic matrix of biological samples for trace metal analysis by atomic spectrometry has been widely used [1-2]. The theory and practice of microwave digestion have been reported by Kingstom and Jassie [3]. The sample preparation methods for flame AAS determination of Al, Ca, Cu, Cr, Fe, Zn in different types of plant samples were studied by L.H.J. Lajunen [4]. Four closed microwave-based digestion procedures have been tested on biological reference samples (tobacco, peat, rice, vine leaves, milk) for application in the determination of trace elements by inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphic furnace atomic absorption spectrometry (GF-AAS) [5]. The chromium in the sediments and biota of the northen part of the Bothnian Bay, (Finland) was analysed by GF-AAS [6].
In this paper there are presented the trace metal contents of nine elements: Ca, Mg, Fe, Al, Mn, Ni, Cu, Cr and Cd determined in bilberries and lingonberries by using ICP-AES, DCP-AES and GF-AAS. The aim of the study was to investigate the possible environmental contamination of industrial pollution from the Kola Peninsula (Nickel and Monchegorsk). The berry samples were collected on seven gradient sampling lines across Finnish Lapland and some samples were collected from the Russian side. The Lapland Forest Damage Project was established in Finnish Forest Research Institute, Rovaniemi [7]. A gradient approach was selected for use in the project. A total of 126 four-plot clusters were placed on 6 east-west and one north-south oriented lines, so that the inter-cluster distance grows from 4 kilometers in the east to the 32 kilometers in the west. Destructive sampling is carried out on subplots, which are situated on the same stands as the permanent monitoring plots.

Intrumentation. Operation Parameters

A sequential PU 7000 inductively coupled plasma atomic emission spectrometer (Unicam Analytical Systems, Cambridge, England) was used for the measurements. The design of this spectrometer includes a 40.68 MHz free-running oscillator for driving the plasma, an echelle grating for the wavelength separation and a grid nebulizer for the sample aspiration. The spectrometer is equipped with a Gilson 221 Autosampler and is controlled by a Philips P 3230 computer [8].
For the determination of Ni, Cu and Al a direct current plasma atomic emission spectrometer SpectraSpan IIIB (Beckman) was used. The determination of very low concentrations of Cd, Cr and Ni was carried out with a Perkin-Elmer Zeeman 3030 graphite furnace atomic absorption spectrometer equipped with a Perkin-Elmer AS-60 Autosampler. The operation parameters and measuring wavelengths are summarized in Table 1 and 2.

TABLE 1

Operation Parameters for the Sequential ICP-AES and DCP-AES

Parameters	ICP-AES	DCP-AES
Plasma power	1.0 kW	approx. 280 W
Coolant flow	13 $dm^3 min^{-1}$	
Sample uptake	1.0 $cm^3 min^{-1}$	2.0 $cm^3 min^{-1}$
Nebulizer pressure	40 psi (28/kPa)	
Read delay	30 s	manual operation
Integration time	3 s	3 s
Number of integration	3	3

TABLE 2

Analytical Operation Conditions and Furnace Program of GF-AAS

Parameter	Cd	Cr	Ni
Wavelength, nm	228.8	357.9	232.0
Light source*	HCL	HCL	HCL
Lamp current, mA	6	25	22
Bandpass, nm	0.7	0.7	0.2
Atomisation**	P	P	P
Chemical modificer	MgPd/Mg	-	-

*HCL = Hollow Cathode Lamp
**P = pyrolytically coated graphite tube with total inserted pyrolytic L'vov platform

Reagents

The stock solutions containing 1000 mg dm^{-3} of each element were prepared using the following reagents (pro analysi, Merck): Al metal, $CaCO_3$, $Cu(NO_3)_2 \cdot 3H_2O$, Fe metal, $MgCl_2.6H_2O$, $MnCl_2.4H_2O$, $NiCl_2 \cdot 6H_2O$, Cd metal and $Cr(NO_3)_3 \cdot 9H_2O$. The mixed calibration standards were prepared by serial dilution of the stock solution with water. Concentrated nitric acid (suprapure, Merck) was added to the standard solution to obtain a concentration of 5 % HNO_3 (v/v).

Microwave Sample Preparation

Samples were digested by using a Milestone ML-S-1200 microwave digestion system. The system includes: a microwave unit ML-S 1200, an exhaust module EM 5, and an automatic capping module ACM 100. The system was equipped with PTFE standard vessels SV 140. The full microwave power of the instrument is 1200 W.
Reference materials and berry samples were accurately weighed (0.25±0.0002 g) into digestion vessels and 5 cm^3 concentrated nitric acid (suprapur, Merck) was added. The vessels were sealed and they were heated according to the program (Fig.1).

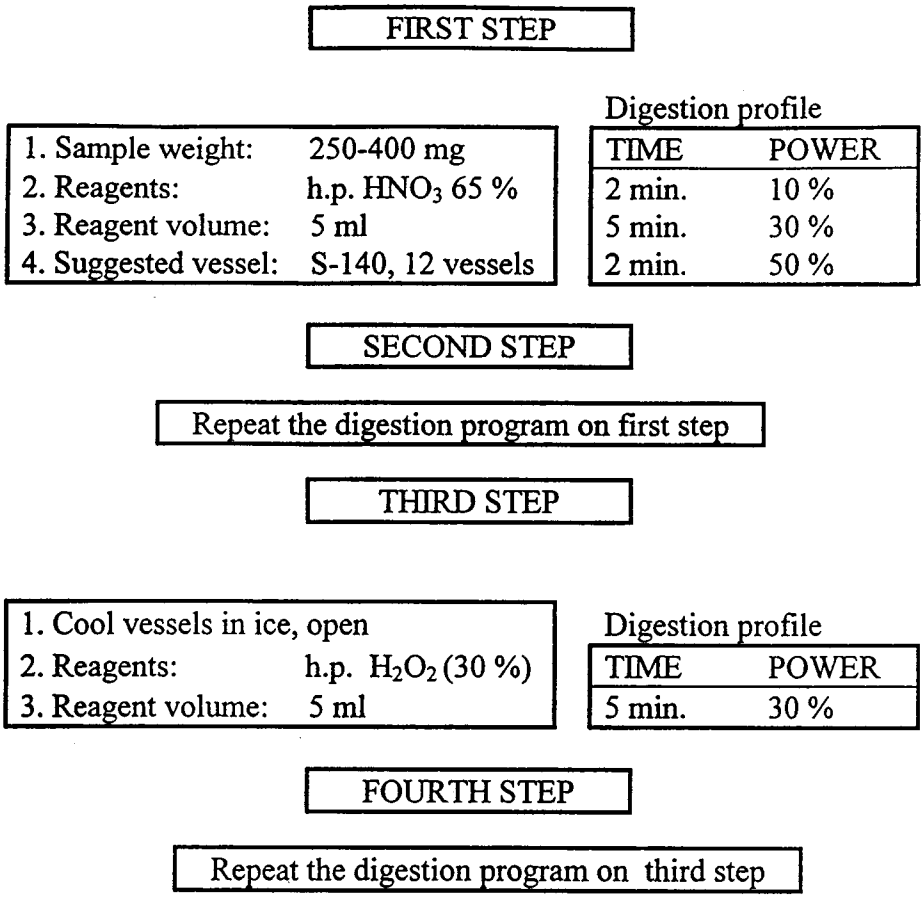

FIGURE 1. Digestion program for berry samples

Results and Discussion

The measuring wavelengths and detection limits are presented in Table 3.

TABLE 3
Wavelengths Used for Various Elements and Detection Limits

Methods	Element, Line*	Wavelength, nm	DL** $\mu g\ ml^{-1}$
ICP-AES	Ca II	317.934	0.08
	Mg I	285.214	0.057
	Fe II	259.940	0.015
	Mn II	258.374	0.017
DSP-AES	Ni I	341.476	0.011
	Al I	396.152	0.025
	Cu I	324.754	0.021
GF-AAS	Cd	228.8	$9.8 \cdot 10^{-5}$
	Cr	257.9	$3.3 \cdot 10^{-4}$
	Ni	232.0	$1.2 \cdot 10^{-3}$

* I atom line, II ion line
** DL=BL+ 3s

The validity of the analytical methods was monitored by analysing two reference materials: Potato Power No. 234 and Wheat Flour No. 137 provided by the ARC Central laboratory of Finland (Table 4)

TABLE 4
Results of Analysis of Reference Materials

Elements	Potato Power 243		Wheat Flour 137	
	Recommended, $\mu g\ g^{-1}$	Found*, $\mu g\ g^{-1}$	Recommended, $\mu g\ g^{-1}$	Found*, $\mu g\ g^{-1}$
Ca	91±6.0	88±5.1	210±5	196±11
Mg	747±16	763±23	570±20	553±24
Fe	22.0±2	19.6±1.7	51.0±6.05	48.8±4.2
Mn	8.1±0.32	7.8±0.25	13.0±0.32	12.6±0.54
Al	-	2.1±0.18	-	4.0±0.32
Cu	3.87±0.18	4.2±0.53	2.48±0.31	2.60±0.03
Ni	0.193±0.043	0.154±0.04	0.12±0.03	0.14±0.04
Cr	0.096±0.018	0.096±0.021	-	0.055±0.01
Cd	0.035±0.0016	0.040±0.005	0.039±0.004	0.044±0.009

* Twelve replicates

TABLE 5
Elemental Composition of the Berries, $\mu g\ g^{-1}$ (dry weight)

Elements	Lapland		Kola	
	Bilberry n = 204	Lingonberry n = 150	Bilberry* n = 16	Lingonberry** n = 8
Ca	1744	1586	1422	1699
Mg	705	681	560	689
Fe	25	14	16.0	21
Mn	471	323	332	326
Al	23.6	24.0	23.8	231
Cu	6.9	6.2	11.5	10.7
Ni	0.90	0.55	9.2	7.5
Cr	0.07	0.08	0.06	0.09
Cd	0.012	0.010	0.007	0.009

* Collected near Nickel
**Collected near Monchegorsk

$$\bar{c}(\text{wet weight}) = \frac{\bar{c}(\text{dry weight})}{8.4} \quad \text{for bilberry samples}$$

$$\bar{c}(\text{wet weight}) = \frac{\bar{c}(\text{dry weight})}{6{,}8} \quad \text{for lingonberry samples}$$

204 bilberry and 150 lingonberry samples collected from Finnish Lapland were analyzed. Some lingonberry samples were gathered near Monchegorsk and Nickel. The results of the analysis calculated on $mg\ kg^{-1}$ dry weight are presented in Table 5.

The heavy metal contents of berry samples gathered from East-Lapland were not higher than those of gathered from West-Lapland. The amount of nickel in lingonberries near Monchegorsk (two sites) was 40 times higher than the average one for Finnish Lapland. The amount of copper was five times higher and the amount of manganese was diminished close to Monchegorsk. On the other hand the analysed heavy metals are not accumulated so well to these berries, so the low concentration measured dos not give the correct picture of the condition of soil.

Acknowledgements

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