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DETERMINATION OF MAJOR ELEMENTS IN LAKE AND RIVER BOTTOM SEDIMENTS BY PHILIPS P.W. 1220 C X-RAY FLUORESCENCE SPECTROMETER

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INTRODUCTION

Within the last twenty years, geochemistry has entered a new era owing to the development of new rapid and accurate analytical techniques, together with the development of the computer. X-ray fluorescence spectrometry is now widely accepted as a highly versatile and potential accurate method of instrumental elemental analysis of geological material. With appropriate excitation techniques, elements can be made to emit light in the X-ray wavelength region, and these radiations can be used to identify and estimate the concentration of elements in samples. In X-ray fluorescence spectrometry excitation of characteristic X-rays is by means of a primary X-beam. From the many publications on theory and practice of X-ray spectrometry, the two following publications are recommended for understanding the principle of this analytical technique: Practical X-ray spectrometry by R. Jenkins and J.L. de Vries (published by Springer-Verlag, New York Inc., 1972) and X-ray Fluorescence Spectrography by K. Norrish and B.W. Chapel, in J. Zussman (Ed.), Physical Methods in Determinative Mineralogy (Academic Press, London), p. 161-214.

A Philips PW 1220 C fully automatic X-ray spectrometer is used for determination of major elements (Si, Al, Ca, Mg, K, Na, Ti, Mn, Fe, and P) in lake and river bottom sediments at Canada Centre for Inland Waters, Process Research Division, Geology Section. X-ray fluorescence analysis comprises the preparation of special pellets, in our case using bottom sediment samples.

EXPERIMENTAL

Sample preparation

(a) Grinding -

The wet sediment sample (sample size is dependable on the water content and should be large enough to yield approximately 7 g dry weight of sediment) is freeze dried and stored in a labeled plastic vial. To remove shell material, plant residues, etc., the dry sediment sample is passed through a 20-mesh (840 μ) screen. Sieved samples are further ground in an agate dish of an automatic grinder (Siebtechnik, West Germany) to pass a 250-mesh (56 μ) screen. After grinding of each sample, the agate dish and its parts are washed with distilled water followed by a methanol rinse and must be completely dry before inserting the next sediment sample. The ground samples are stored in labeled plastic vials tightly closed.

(b) Pelletizing -

6.0 g of a sediment sample is weighed in a 16 dram labeled plastic vial and 1.0 g of thermo-setting phenol formaldehyde resin (Bakelite Co. Ltd., Toronto) is added to it. The smallest amount of sample essential for making a pellet is 3.0 g of sediment sample and 0.5 g of binding resin. Two glass beads (1 cm diam., Spex Industries, Inc., Metuchen, N.Y.) are placed in the vial containing the sample-resin mixture. The mixture in the vial is then homogenized for 5 min, in a mixer/mill (Spex Industries, Inc.). The mixture is spooned by spatula into a 32 mm diameter aluminium cup (Spex Industries, Inc.) and pressed into a pellet under a pressure of 30 tons for 5 min (Leake et al. 1969) in an automatic pelletizer (Herzog, West Germany). The

sample pellet is kept, preferably, in a desiccator or in a closed box, at room temperature, before analysis by X-ray fluorescence spectrometer.

STANDARDS

Great Lakes bottom sediments were chosen as standards for the X-ray fluorescence spectrometry analysis. These standard samples were ground and pelletized as described above. The pellets are stored in a desiccator and used regularly. The pulverized standards were analyzed for the above-mentioned major elements using rapid USGS wet chemical methods. The results were checked by comparison with analysis of the USGS standard rocks G2, PCC1 and DTS1 (Cronan and Thomas, 1972).

COMPUTER PROGRAMS AND CALCULATIONS

The computer program for control of PW 1220 C spectrometer and for calculation of the weight percent of major elements by using the intensity correction method was supplied by Philips Co. and is referred to as XRAY-20. The program consists of six parts,, each supplied on a separate tape. For the analysis of sediment samples, the first part (XRAY-20A) of the program is used, which controls the PW 1220 C spectrometer and reads out the measured results, calculates the weight percent

from the measured intensities and punches out the assembled analytical parameters on a paper tape. The preparation of this program is described in detail in "Directions for use of computerized spectrometer PW 1220", supplied by Philips Co.

ANALYTICAL CONDITIONS

Element	Channel	2Ø	KV	MA	Collimator	Crystal	Detector	Time
1. Ti	3	36.33	60	32	Fine	EDDT	Flow	20 sec
2. Mg	5	43.50	60	32	Fine	KAP	Flow	100 sec
3 MgB[1]	6	42.91	60	32	Fine	KAP	Flow	100 sec
4. Ca	4	44.50	60	8	Fine	EDDT	Flow	20 sec
5. K	8	50.22	60	32	Coarse	EDDT	Flow	20 sec
6. Na	10	53.06	60	32	Coarse	KAP	Flow	100 sec
7. NaB[1]	11	54.08	60	32	Coarse	KAP	Flow	100 sec
8. S	16	75.18	60	32	Coarse	EDDT	Flow	80 sec
9. Fe	17	85.65	60	32	Fine	LIF 220	Flow	20 sec
10. P	18	88.78	60	32	Coarse	EDDT	Flow	100 sec
11. Mn	20	95.11	60	32	Fine	LIF 220	F & S	40 sec
12. Si	21	198.02	60	32	Coarse	EDDT	Flow	20 sec
13. Al	23	142.73	60	32	Coarse	EDDT	Flow	20 sec

Tube: Chromium

1 Mg and Na background values.

After all prescribed preparation procedures of the spectrometer have been completed according to the manual, the computer-spectrometer is ready to do the analysis.

SPECTROMETER OPERATION

The spectrometer is supplied by four sample cups. After start, sample cup No. 1 will be in the sample loading position. This is normally the position for the standard. The standard is inserted and the print button is pushed (without giving an identification number), bringing the next sample cup to the loading position.

A sample is inserted into the PW 1220 C and an identification number is given followed by print.

The identification number is a reference for the computer, on which the samples are inserted. The print command will store the previous given number and will bring the next sample position into the fill opening. To bring a next position in the fill opening, a single print command is given. The identification number is limited to seven decimal numbers. If more are given, the computer will ignore the number and type on the ASR 33 the error message: ⊄02.

When one or more samples have been loaded, the analytical program required is selected with a knob by pressing the computer start button on the PW 1220 C. On receipt of the start command, the computer will check whether or not samples were inserted (e.g. whether identification

numbers were given).

If samples are present, the program number is loaded (1 ... 10) and the parameter list belonging to this program number is brought into the control program. If no list is stored in the computer for this program number, §03 will be typed and the computer will go to stand by. The proper program should be chosen and again the start button pressed.

If the list is available, the "busy" lamp will come on, the vacuum pump will be started and all measuring settings (such as kV, mA, preset time or count, channel, etc.) will be adjusted for the first element.

As soon as the first sample has been measured, the next sample, if present, will be measured for the first element, and so on, until all samples have been measured for this element. Thereafter, the same process will be repeated for the next element of the analytical program.

After reading a result from the spectrometer, the computer will start the next measurement (the next sample on the same element or the first measurement on the next element). The computer then jumps to the calculation program and will compute and output the results as far as possible, i.e., as far as results are available, thereby starting at the position where it stopped the last time because of lack of results being available. The consequence is that the results will be typed out as soon as the relevent measuring result(s) have been read from the computer.

When all measurements have been done, the calculation program will skip interelement corrections and concentration output of elements where no results are available, thus completing the whole calculation program. As soon as all calculations and measurements have been performed,

the vacuum pump is switched off, the filled sample position with the lowest number is brought to the fill opening and the computer goes back to the stand-by position awaiting the next analysis run.

CONCLUSION

The X-ray fluorescence spectrometry method is a sufficiently accurate method for determination of major elements in bottom sediment samples, enabling analysis of approximately 24 pelletized sediment samples during one working day. The advantage of the combination of spectrometer-computer is the simultaneous analysis and complete calculation of the analytical results.

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