QUANTITATIVE DETERMINATION OF MOLYBDENUM, NICKEL, VANADIUM AND TITANIUM IN THE ASPHALTITES AND ASPHALTITE ASHES BY XRF-SPECTROSCOPY

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ABSTRACT. — The quantitative determinations of Mo, Ni, V and Ti in the asphaltite occurrences of Southeastern Turkey and in their ashes as well have been made by XRF spectroscopy. The matrix effects in the analyses of these elements have been minimised by employing Nb, Co, Ce and La as internal standards, corresponding to Mo, Ni, V and Ti respectively.

1. INTRODUCTION AND BACKGROUND INFORMATION

Recovery of valuable minerals, i.e.Mo, V, Ni, and Ti contained in the asphaltites and their ashes and synthetic gas, liquid and solid fuels as well by pyrolysis have been investigated by the M.T.A. Institute with a purpose to evaluate the asphaltite occurrences of Southeastern Turkey (1). XRF (X-ray fluorescence) spectroscopy is employed for qualitative analyses, to minimise the amount of samples used and to reduce the testing period.

The method employed in the matrix corrections and in the selection of internal standards taken into consideration in the present study is described in reference (2).

2. APPLICATION

During XRF analyses, GE - SPG - 5 vacuum spectrometer arid GE - SPG - 9 gas spectrometer, in which a mixture of 10 % methane and 90 % argon is streamed, are used.

2. 1. Mo, Ni, V and Ti determinations in asphaltites and their ashes

During these studies Nb, Co, Ce and La arc used as internal standards, corresponding to Mo, Ni, V and Ti, respectively, as these minerals have similar wavelengths (3) (Fig. 1). Optical spectrographic studies have, on the other hand, shown that the elements referred above and taken as internal standards in these studies, are not present in the samples.

Table 1 shows the elements determined and the curves obtained for the respective internal standards. No elements, however, emitting characteristic x-rays having necessary intensity to affect the method employed could be identified between or around the curves (4).

Table - 1

Element to be determined			*Internal standard used*		
V	Peak 20$_K$	= 122°.80	Ce	Peak 20$_K$	= 127°.85
	B.G. 20	= 124°.56		B.G. 20	= 132°.00
Ni	Peak 20$_K$	= 70°.80	Co	Peak 20$_K$	= 69°.00
	B.G. 20	= 73°.00		B.G. 20	= 67°.80
Mo	Peak 20$_K$	= 28°.40	Nb	Peak 20$_K$	= 29°.90
	B.G. 20	= 27°.40		B.G. 20	= 30°.90
Ti	Peak 20$_K$	= 85°.70	La	Peak 20$_L$	= 82°.50
	B.G. 20	= 89°.00		B.G. 20	= 81°.00

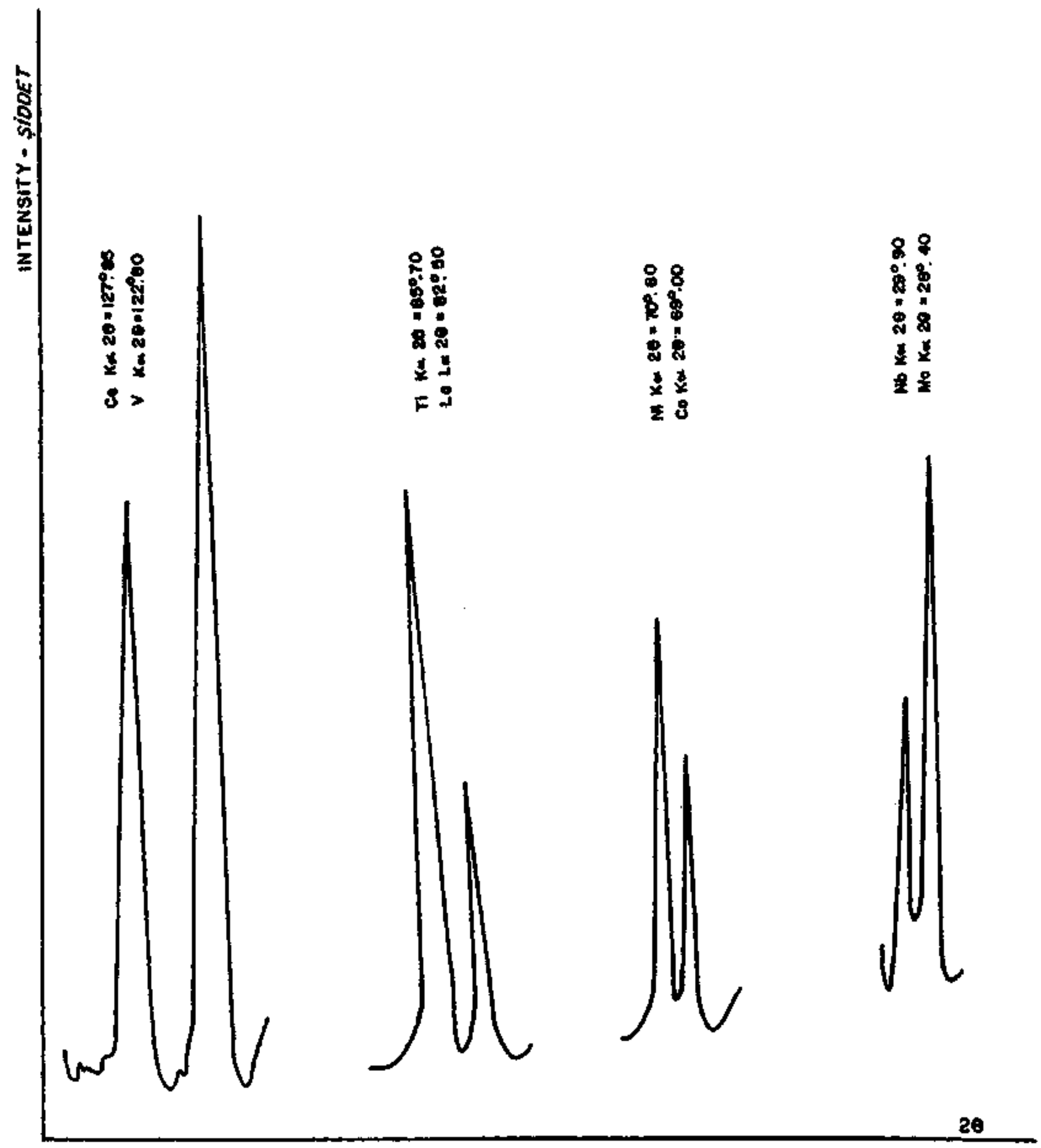

Fig. - 1

2.2. Preparation of standard sample tablets

a. Mo, Ni and V standards. — Mo, Ni and V standard solutions and Nb, Co and Ce internal standards, of variable concentrations are added to 250 mg $Li_2B_4O_7$.5H2O+250 mg SiO2+ 500 mg cellulose mixture. The mixture thus obtained is ground homogeneously after drying at 80°C for one night and sample tablets are made using 25-ton presses.

b. Ti standards. — Ti standards are prepared similarly, with the exception of adding La in solution as an internal standard.

c. Preparation of samples. — During the preparation of samples, the method employed is similar and internal standards are added to a mixture of 250 mg $Li_2B_4O_7.5H_2O$+250 mg sample and 500 mg cellulose by drops.

2.3. Measuring conditions

	Mo	*Ni*	*V*	*Ti*
Crystal (A°)	**Fibre (2.8)**	**Fiber (2.8)**	**Fiber (2.8)**	**Fiber (2.8)**
Anticathod	**W**	**W**	**Cr**	**W**
Flow intensity of tube (mA)	**40**	**40**	**40**	**40**
Tube voltage (kV)	**50**	**50**	**50**	**50**
Interval (inch)	**0.005**	**0.005**	**0.005**	**0.005**
Pressure	**Vacuum**	**Vacuum**	**Vacuum**	**Vacuum**
Counter voltage (V)	**1250**	**1330**	**1370**	**1300**
Discrimination limit (V)	**20-60**	**30-50**	**30-60**	**10-40**
Counting time (sec.)	**20**	**20**	**20**	**20**

3. EVALUATION OF RESULTS

Results are evaluated on the basis of the following equation (2) and seperate curves are obtained for each element (Fig. 2).

$$\frac{I - Io}{Is - Ios} = KC$$

Where;

I is the intensity of the secondary x-rays emitted by the sample at the measured wavelength;

lo natural background around the measured wavelength;

Is intensity of the x-rays emitted by the internal standard at the measured wavelength;

los natural background of the internal standard;

K Constant

C Concentration of the element to be analysed in the sample.

Table 2 shows the Mo, Ni, V and Ti percentages of the asphaltite, asphaltite ash, resulting carbonaceous residue and ash as well, determined by the method described above.

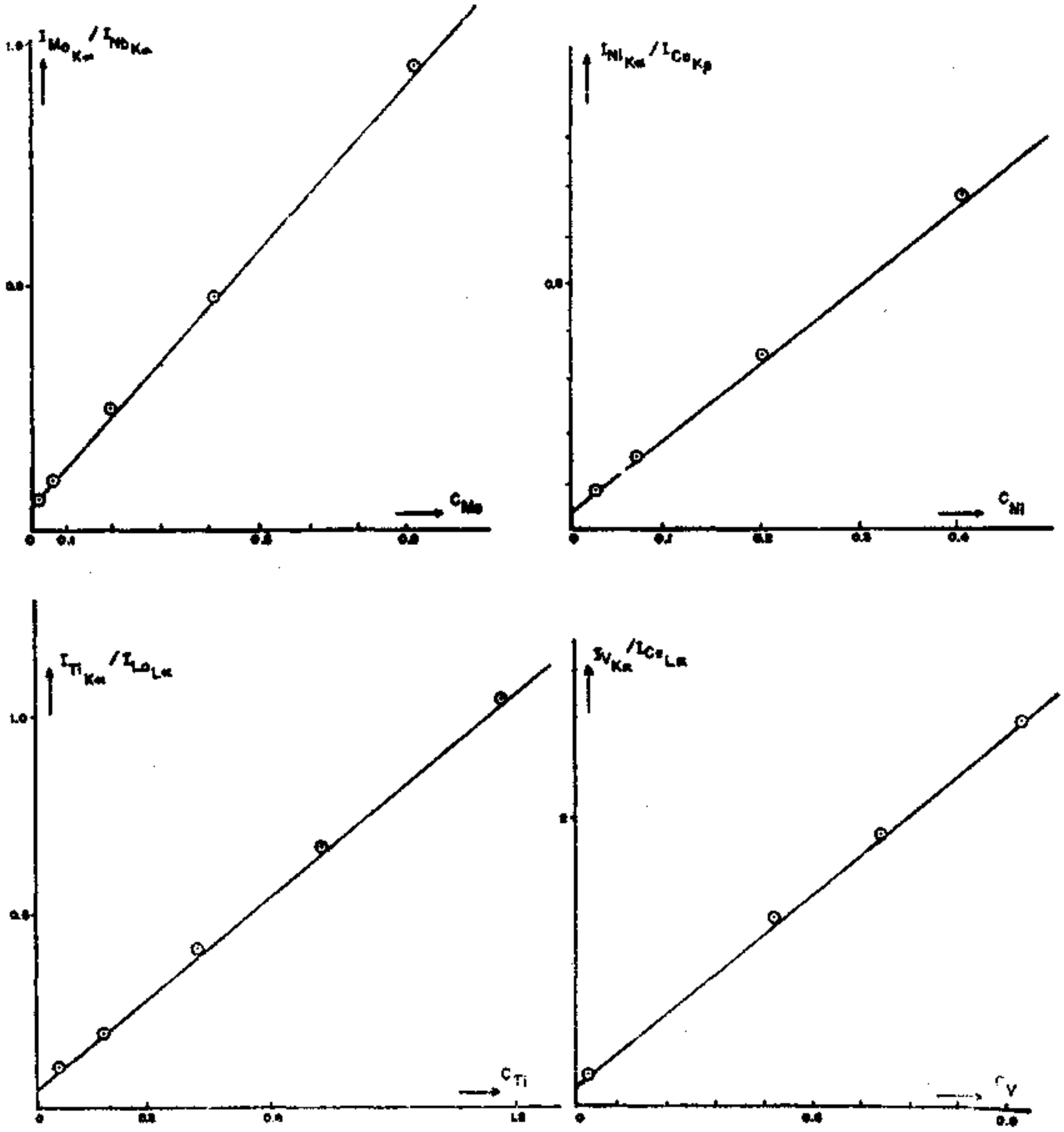
$I_{Mo_{K\alpha}} / I_{Nb_{K\alpha}}$
1.0
0.5
0
0.1
0.5
0.8
C_{Mo}
$I_{Ni_{K\alpha}} / I_{Co_{K\beta}}$
0.5
0
0.1
0.2
0.3
0.4
C_{Ni}
$I_{Ti_{K\alpha}} / I_{La_{L\alpha}}$
1.0
0.5
0
0.2
0.4
0.8
C_{Ti}
$I_{V_{K\alpha}} / I_{Ce_{L\alpha}}$
2
0
0.5
0.9
C_V

Fig. - 2

Table - 2

Element	*Asphaltite* (%)	*Asphaltite ash* (%)	*Pyrolysis coke* (%)	*Pyrolysis coke* ash (%)
Mo	**0.13**	**0.29**	**0.18**	**0.31**
Ni	**0.15**	**0.33**	**0.18**	**0.35**
V	**0.15**	**0.35**	**0.18**	**0.35**
Ti	**0.14**	**0.33**	**0.13**	**0.33**

Absolute error : ± 0.01

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