EXTENDED SOFTWARE POSSIBILITIES IN X-RAY MICROANALYSIS

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Résumé - En microanalyse par rayons X, de nouvelles possibilités intéressantes d'application de l'informatique ont été développées au cours de ces dernières années. Quelques-unes d'entre elles, à savoir notamment les programmes QLA, TRACE, MAP et CALIB, sont décrites ci-après. Elles relèvent de l'utilisation, dans le domaine de la métallurgie, d'une microsonde électronique "JEOL Superprobe JXCA-733" pilotée par ordinateur.

Abstract - In recent years further interesting computer application in X-ray microanalysis have been developed. Some of these (QLA-, TRACE-, MAP- and CALIB-program) will be presented using a computer controlled electron microprobe "JEOL Superprobe JXCA-733" for metallurgical applications.

QLA-program

This program makes it possible to check within a few minutes for the presence of totally 71 elements ranging from fluorine to uranium, and to print out the results in a hardcopy. In QLA-program, three channels [CH(1) to CH(3)] of spectrometers are scanned over their entire range and X-intensities of the mentioned elements are measured at the points corresponding to the caracteristics emission lines. An important advantage of the energy dispersive method over wavelength dispersive systems has previously been the speed with which a general qualitative analysis could be obtained. This gap can now be closed for wavelength dispersive spectrometers by using the QLA-program, through which comparable detection limits can be attained (see Table I). The substantially higher energy resolution of the crystal spectrometer system also represents a great advantage, especially with a view to increasing analytical certainty. Rapid qualitative analyses with the aid of the QLA-program are to be recommended in the field of metallurgy above all for the investigation of slags (Fig. 1), corrosion products, metal chips etc.

Element	X-ray line	mass-%	Element	X-ray line	mass-%
Al	K_α	0.08	Cr	K_α	0.2
Si	K_α	0.08	Mn	K_α	0.2
P	K_α	0.3	Co	K_α	0.2
S	K_α	0.3	Ni	K_α	0.1
Ti	K_α	0.4	Mo	L_α	0.6
V	K_α	0.3	W	L_α	0.4

Table I - Detection limits in mass-% for selected steel elements by means of QLA-program for an accelerating voltage of 25 kV and a probe current of 10^{-8}A. (The dectection limits may be improved by using higher probe currents.)

PROBE CURRENT : 2.060E-08 (A)
STAGE POS. : X 13567 Y 22904 Z 11407

	CH(1) TAP				CH(2) PET				CH(3) LIF			
EL	WL	COUNT	INTENSITY(LOG)	EL	WL	COUNT	INTENSITY(LOG)	EL	WL	COUNT	INTENSITY(LOG)
Y	6.45	62	**********	I	3.15	29	********	BR	1.04	54	**********+
RE	6.73	98	***********	TE	3.29	20	*******	TL	1.21	54	**********+
SR	6.86	94	***********	CA	3.36	95	**********+	GE	1.25	41	**********
SI	7.13	11148	************************+++++	SB	3.44	24	*******	PT	1.31	40	**********
RB	7.32	74	**********	SN	3.60	21	*******	IR	1.35	38	**********
LU	7.84	53	*********	K	3.74	359	**************+	OS	1.39	36	**********
YB	8.13	50	*********	IN	3.77	14	******	W	1.48	28	*********
AL	8.34	3940	********************+++++	U	3.91	10	*****	TA	1.52	26	*********
ER	8.82	34	********	CD	3.96	11	******	HF	1.57	28	*********
SE	8.99	25	********	TH	4.14	8	*****+	NI	1.66	34	*********+
HO	9.20	27	********	AG	4.15	10	*****	TM	1.73	16	*******
DY	9.59	18	*******	PD	4.37	9	*****	CO	1.79	18	*******
AS	9.67	16	*******	RH	4.60	3	***	FE	1.94	2843	********************+
MG	9.89	42	*********+	CL	4.73	7	**+	GD	2.05	11	******
TB	10.00	9	*****+	RU	4.85	1	*	MN	2.10	461	**********+++++
EU	10.96	6	****	BI	5.12	1	+	CR	2.29	36	*********+++
BA	11.29	5	****+	PB	5.29	1	*	PR	2.46	5	***++
SM	11.47	3	***	S	5.37	1	+	V	2.50	3	***
NA	11.91	5	****+	MO	5.41	0		CE	2.56	4	****+
ZN	12.25	5	****+	HG	5.65	0		LA	2.67	4	****+
ND	12.68	2	**	NB	5.72	0		TI	2.75	4	****+
CU	13.34	4	***+	AU	5.84	1	*	BA	2.78	3	***
**	15.80	0		ZR	6.07	0		CS	2.89	1	*
F	18.32	0		P	6.16	0		SC	3.03	1	*

DER LOG. AUSDRUCK UNTERSCHEIDET ZWISCHEN UNTERGRUND (*) UND ELEMENT (+)

RESULTS:

THE FOLLOWING ELEMENTS ARE PRESENT

MG, AL, SI, K, CA, CR, MN, FE, NI

Fig. 1 - QLA-analysis of slag in steel. Accelerating voltage 25 kV, probe current 10^{-8}A.

For high-speed quantitative analysis recently a new semi-quantitative analysis program was developed which is aimed at performing qualitative analysis and obtaining the approximate results of quantitative analysis at high speed without requiring measurement of the specific standard specimen for the elements detected [1].

TRACE-program

This computer controlled measuring process samples automatically within a certain wavelength range of the X-ray spectrum using a spectrometer at high precision and with a minimum step of 1 micron. By this means even very low concentration (down to the ppm range) can be clearly established statistically. A typical, relevant practical example of this process is the detection of nitrogen when investigating stress corrosion cracking on brass. As Fig. 2 shows, the corrosion products on an opened fracture surface with small amounts of nitrogen (approx. 0.2 mass-%) reveal with the aid of the TRACE-program clearly the presence of the N K-emission band, whereas this element could not be detected at any of the points investigated when the process was not controlled by a computer.
Furthermore this program also represents a useful procedure for examining the influence of chemical bonding on the X-ray emission spectra. Fig. 3 shows a representation of the measured data for the investigation of the S Kβ-emission bands emitted by FeS_2 and $FeSO_4$. The clear band separation makes it possible for corrosion investigations to determine within a short time (approx. 5 min) the degree of oxidation of the elements S or Fe contained in the corrosion products and thus to draw more precise conclusions concerning the corrosion mechanism. This applies especially in the case of corrosion phenomena at locally limited areas where other methods (X-ray fluorescence analysis, X-ray diffraction, wet chemical methods) cannot be used.

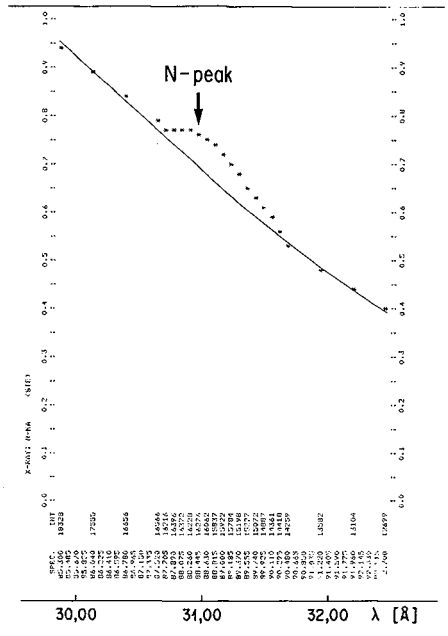

Fig. 2 - Microanalytic evidence of bound nitrogen (nitrogen concentration approx. 0.2 mass-%) in the corrosion products $[Cu(NH_3)_4(OH)_2]$ on the opened fracture surface, determined by means of N K-emission band. Analyser crystal STE, accelerating voltage 10 kV, probe current 3.10^{-6} A, spectrometer step 185 µm (approx. 0.065 Å), meas. time/per step 10 s.

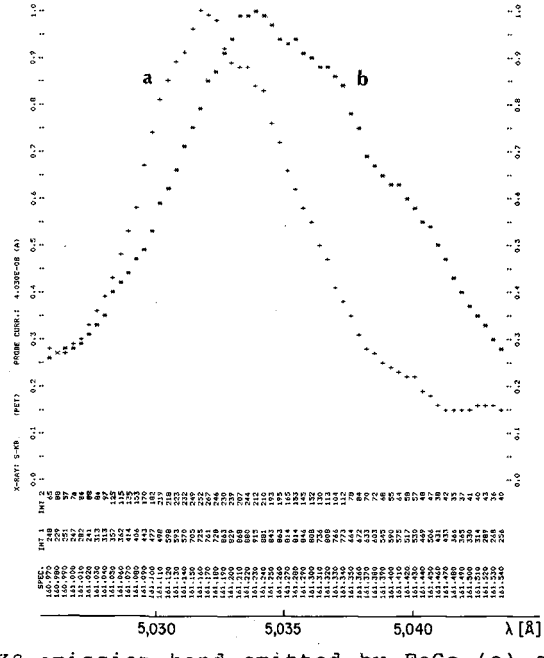

Fig. 3 - The S Kβ-emission band emitted by $FeSo_4$(a) and FeS_2(b). Analyser crystal PET, accelerating voltage 15 kV, probe current 4.10^{-8}A, spectrometer step 10 µm (approx. 0.0003 Å), meas. time/per step 2 s.

MAP-program

The program produces at various magnifications highly accurate two dimensional X-ray contour maps, with the additional possibility of evaluating these digital element maps semi-quantitatively over the entire concentration range. This allows interesting metallurgical investigations, such as of segregation phenomena respectively diffusion zones.

CALIB-program

In special cases, the CALIB-computer-program enables the user to obtain more precise analytical results through the use of calibration curves than would be possible with the usual ZAF programs and the application of pure standards. One of its most important applications in the field of metallurgy is the analysis of the carbon content in steels, for example, when investigating case-hardened layers. The concentrations which appear in this context (for the most part, between 0.1 and 1.0 mass-%) cause substantial difficulties with the usual ZAF corrections. By using the CALIB-program and special standard steel specimens, the carbon analysis is simplified considerably and its accuracy improved.

References

[1] ONO Y., JEOL NEWS 21E, n°1 (1983) 9.