Application Note

ICP ATOMIC EMISSION SPECTROSCOPY

APPLICATION NOTE 46

MASTER Assistance for Impurity Analysis in a Nb/Ni/Zr Matrix

Jean-Claude Birolleau, CEA Le Ripault, Monts, France
Agnès Cosnier, ICP Product Manager, HORIBA Scientific, Longjumeau, France

Keywords: Software tools, line search, method development

1 Introduction

The ACTIVA-M ICP-AES instrument allows the operator to easily achieve the high reliability of results that every analyst wishes based on the concept of total multi-line analysis.

Multi-line analysis makes the detection of outliers possible, thereby coping with unexpected spectral interferences and, consequently, improving the reliability of final results. However, the concept of selecting several lines per element complicates method development.

The solution that HORIBA Scientific proposes with the ACTIVA-M is assistance via specific software tools. Among them, the MASTER: Multi-line Analysis, Selection Tool for Enhanced Reliability.

2 Presentation of MASTER(1)

The objective of the MASTER tool is to help the operator in the selection of appropriate lines according to a defined application (matrix, elements and concentrations), and to control any resulting spectral interferences.

The essence of MASTER is the S^3-base (Single-element Spectra, Spectroscopic data), a real ICP-based data base with dual access that has been developed by HORIBA Scientific. It is a collection of single-element spectra (acquired on an ACTIVA-M instrument, at different concentrations, for all elements) and a data base containing wavelengths, ionisation state, excitation energy, sensitivity, background level, limit of detection, maximum concentration below detector saturation and line width. More than 50,000 lines have been assigned.

Once the application is defined in MASTER by the user (list of elements and range of (expected, average) concentrations), the Filtering procedure is automatically applied and addresses a list of appropriate lines in terms of concentration range and interferences. The Filtering consists of controlling the main criteria of sensitivity, maximum concentration and interference from S^3-base spectroscopic data. A Display procedure allows the analyst to verify the lines and set up background correction positions, thanks to the over-lapping of the blank spectrum and of single-element spectra of all elements of interest at the defined concentrations.

The method development is consequently faster as it does not require any standard solution preparation and any profiling. The following diagram illustrates the elements required for method development with and without the MASTER help:

Without MASTER	**With MASTER**
- Matrix identification	- Matrix identification
- Elements and concentration range definition	- Elements and concentration range definition
- ICP-AES	- Computer
- Preliminary selection of wavelengths according to concentration range (from tables)	
- Single-element standards preparation	
- Solution profiling at selected wavelengths	
- Control of spectral interferences	
- New wavelengths selection and profiling if needed	

3 MASTER Assistance

The analytical application is described in the following Table 1:

Table 1: Analytical application

Matrix	Ni 70-80 % weight Nb 4-6 % weight Zr 15-25 % weight	Concentration provided by the customer
Impurities	Cr, Fe, Mo, Ti	Determine feasability

Both major elements from matrix and impurities must be analysed, leading to two different sample preparations.

Two programs are then set up in MASTER.

- **Major elements**

The concentration range for the majors is defined as follows (mg/L):

	LCL	UCL
Nb	2.5	3.8
Ni	40	50
Zr	13	16

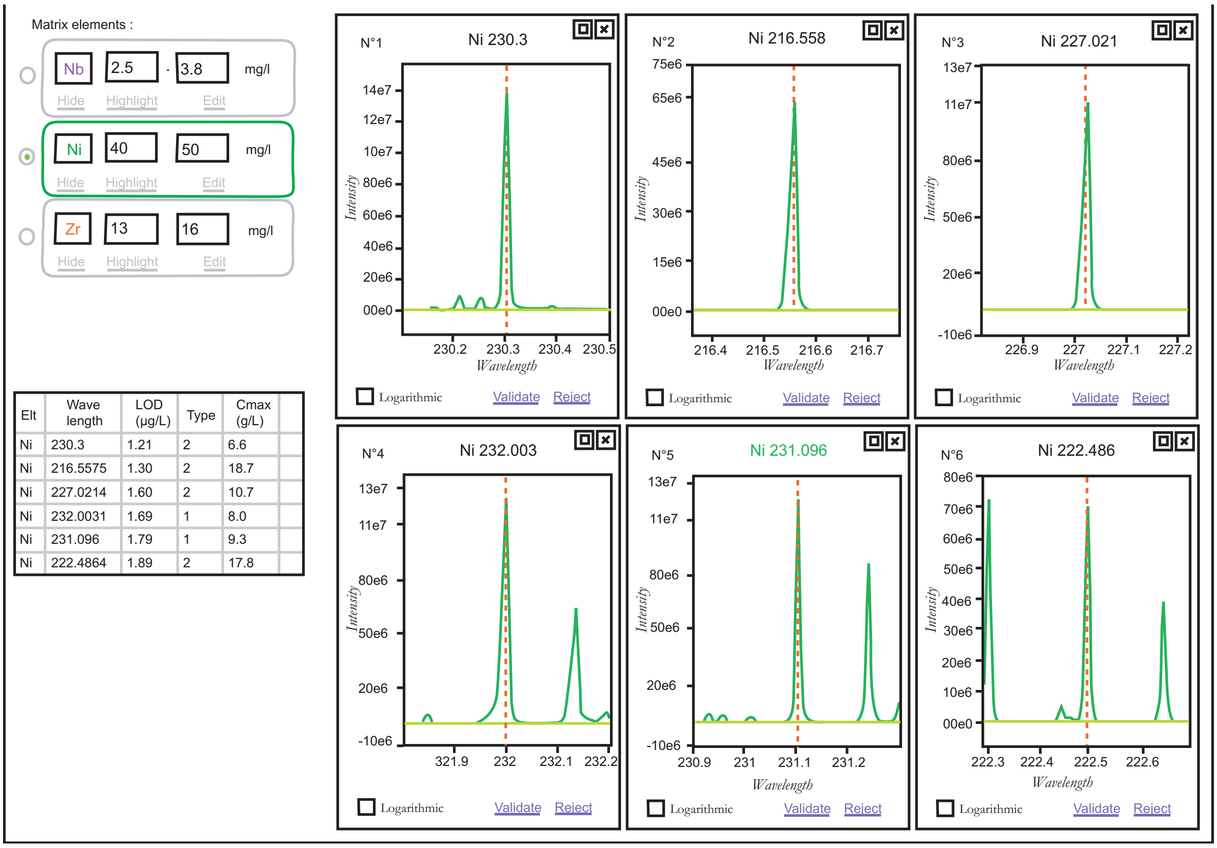
With LCL: Lower Concentration Limit and UCL: Upper Concentration limit.

MASTER applies the Filtering procedure in order to propose an appropriate lines (for this application, n = 6) according to concentration range and interference criteria.

Each line proposed is then displayed: spectrum of the analyte at its minimum concentration together with the single-element spectra of concomitant elements at their maximum concentration (to simulate the most pessimistic case).

The display allows the analyst to control the line and its vicinity and to decide for on validation or rejection. The display also permits to applying background correction positions.

The Figure 1 below illustrates the MASTER screen when Ni is selected: the 6 lines proposed are listed with some spectroscopic data (Limit Of Detection (LOD) and maximum concentration below saturation (Cmax)) and are displayed individually in a graph.



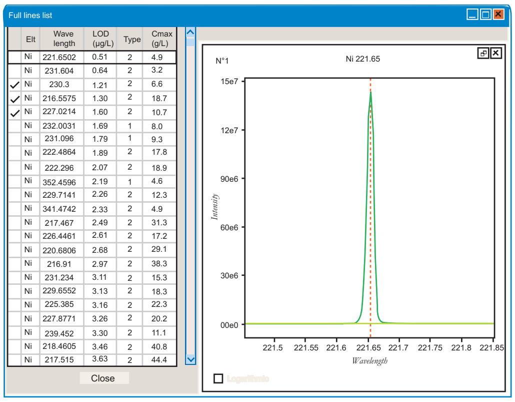
Matrix elements :

○ Nb 2.5 - 3.8 mg/l
● Ni 40 50 mg/l
○ Zr 13 16 mg/l

Elt	Wave length	LOD (µg/L)	Type	Cmax (g/L)
Ni	230.3	1.21	2	6.6
Ni	216.5575	1.30	2	18.7
Ni	227.0214	1.60	2	10.7
Ni	232.0031	1.69	1	8.0
Ni	231.096	1.79	1	9.3
Ni	222.4864	1.89	2	17.8

Figure 1: List and graphs of lines for Ni

When we access to the full list of Ni lines, we observe that the first two lines were not selected (Figure 2). In the Filtering procedure, there is a criterion on Cmax, which factor was fixed at 100, to get Cmax > UCL x 100. This criterion is important for major analysis. In the example here, the sensitive line 231.604 nm has a Cmax of 3.2 g/L and was thus not selected by MASTER.



Full lines list

	Elt	Wave length	LOD (µg/L)	Type	Cmax (g/L)
	Ni	221.6502	0.51	2	4.9
	Ni	231.604	0.64	2	3.2
✓	Ni	230.3	1.21	2	6.6
✓	Ni	216.5575	1.30	2	18.7
✓	Ni	227.0214	1.60	2	10.7
	Ni	232.0031	1.69	1	8.0
	Ni	231.096	1.79	1	9.3
	Ni	222.4864	1.89	2	17.8
	Ni	222.296	2.07	2	18.9
	Ni	352.4596	2.19	1	4.6
	Ni	229.7141	2.26	2	12.3
	Ni	341.4742	2.33	2	4.9
	Ni	217.467	2.49	2	31.3
	Ni	226.4461	2.61	2	17.2
	Ni	220.6806	2.68	2	29.1
	Ni	216.91	2.97	2	38.3
	Ni	231.234	3.11	2	15.3
	Ni	229.6552	3.13	2	18.3
	Ni	225.385	3.16	2	22.3
	Ni	227.8771	3.26	2	20.2
	Ni	239.452	3.30	2	11.1
	Ni	218.4605	3.46	2	40.8
	Ni	217.515	3.63	2	44.4

Figure 2: List of all Ni

Figure 3 shows all the single-element spectra for the Ni 230 nm line. In case of a higher concentration of Zr in one sample, this line may be interfered and the analyst can decide then to reject this line proposed by MASTER. Figure 4 shows a validated line and the positions of background correction that have been selected.

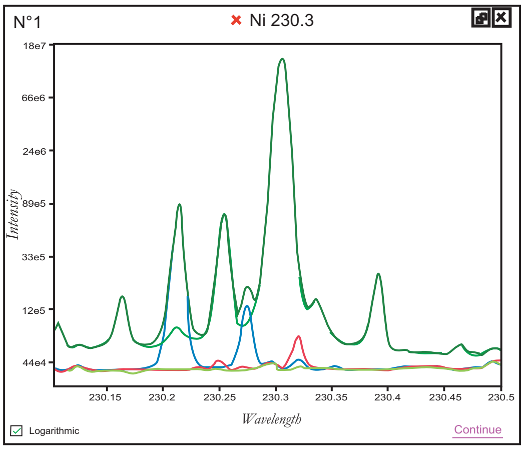


Figure 3: Ni 230 nm line is rejected by the user

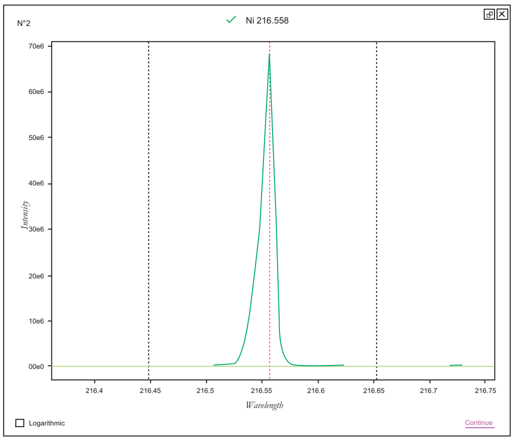


Figure 4: Ni 216 nm line is validated by the user

The MASTER selection and the visualisation procedure leads to the final selection of lines as follows:

Nb	316.340 / 309.418 / 295.088 nm
Ni	216.556 / 231.096 nm
Zr	256.887 / 274.256 nm

The method for major analysis was rapidly (a few minutes) created without any data acquisition. The program developed in MASTER can then be exported directly to the ACTIVAnalyst software. After optimisation of acquisition parameters, the method is then ready for calibration and analysis.

• Impurity elements

The same procedure is applied for impurities.

	LCL	UCL
Cr	0.1	0.15
Fe	0.1	0.15
Mo	0.1	0.15
Ti	0.1	0.15

For this program, the major elements are also defined, as they constitute the matrix (10 times more concentrated than in the previous example, to improve visibility):

	LCL	UCL
Nb	25	38
Ni	400	500
Zr	130	160

Once concentration ranges are defined, the Filtering is applied. For traces, the criterion of sensitivity is of a great importance: each line proposed should have a LOD which follows the formula LOD x k < LCL (k is user-defined and is fixed here at 10).

After visualisation of the graphs for the lines proposed by MASTER, the final selection for the trace elements is:

Cr	206.562 / 286.257 nm
Fe	239.563 / 240.489 nm
Mo	202.030 / 204.598 nm
Ti	323.904 / 337.280 nm

4 Real experiments on ACTIVA-M

Profiles from single-element solutions were acquired on ACTIVA-M for validated lines and some rejected lines, and then compared to the synthetic spectra reconstituted in MASTER (from the Single-element Spectra stored in the S^3-base) which were used for visualisation and decision. The perfect agreement illustrates how efficient the MASTER tool is.

Figures 5 and 6 are respectively examples for the Cr 286 nm line that was previously validated and the Ti 323 nm line that was rejected.

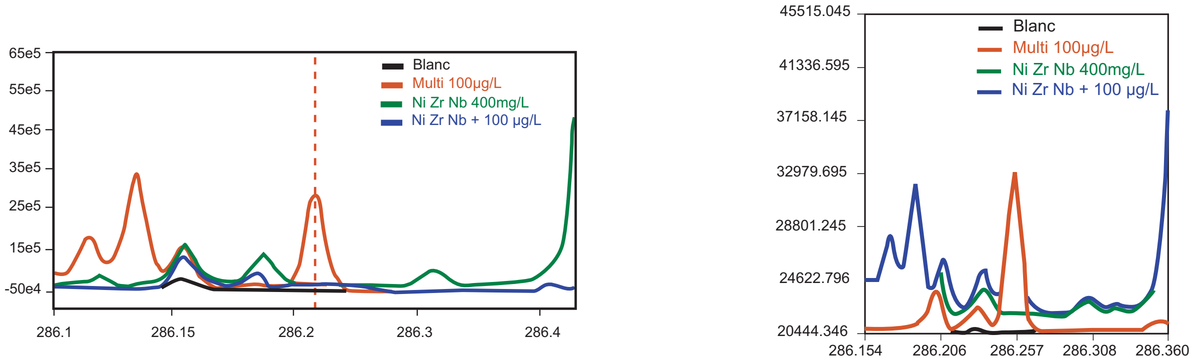


Figure 5: Cr 286.257 nm line (left: MASTER, right: ACTIVAnalyst)

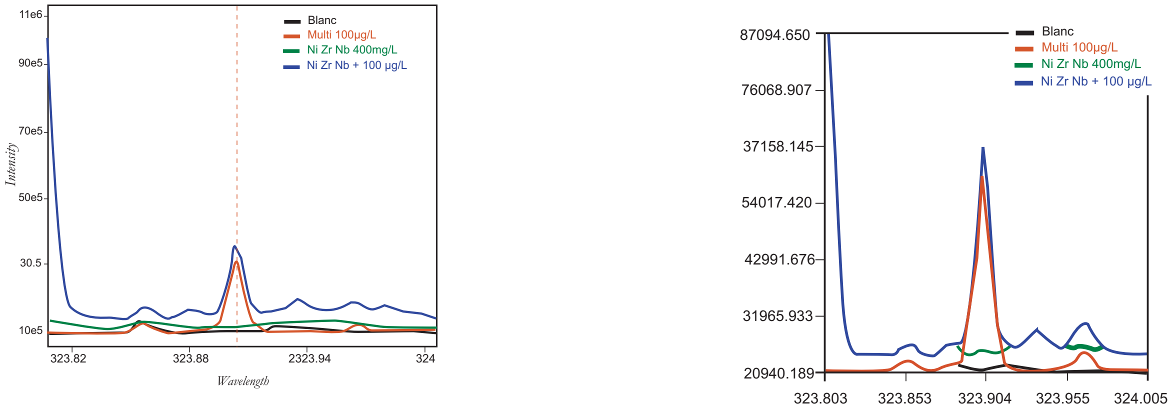


Figure 6: Ti 323.452 nm line (left: MASTER, right: ACTIVAnalyst)

7 Conclusion

With the condition that all the major elements to measure and their concentration range are well known (otherwise, a semi-quantitative analysis – IMAGE or an XRF analysis for example – is recommended for identification), the MASTER tool offers an automatic selection of lines which saves development time (no solution preparation, no search in wavelength tables, no profiling) and offers interactivity to the user. It can be operated off-line (no need of computer connected to the ICP-AES instrument). The program can be easily optimised at any time if the nature of the samples varies (change in concentration of a matrix element, new element to measure…).

An export of the program to the ACTIVanalyst software ensures fast analytical method creation. There is no need for line profiling neither to confirm the selection nor applying background correction. The method is straight operational.

[1] ACTIVA-M brochure, HORIBA Scientfic, www.horiba.com/scientific

info-sci.fr@horiba.com
www.horiba.com/scientific

France: HORIBA Jobin Yvon S.A.S., 16-18 rue du Canal, 91165 Longjumeau Cedex - Tel: +33 (0)1 64 54 13 00 - Fax: +33 (0)1 69 09 07 21 - Email: info-sci.fr@horiba.com
USA: HORIBA Jobin Yvon Inc., 3880 Park Avenue, Edison, NJ 08820-3012. Toll-free: +1-866-jobinyvon - Tel: +1-732-494-8660 - Fax: +1-732-549-5125
Email: info-sci.us@horiba.com
Japan: HORIBA Ltd., Scientific Instruments Sales Dept., Alte-Building Higashi-Kanda, 1-7-8 Higashi-Kanda, Chiyoda-ku, 101-0031 Tokyo - Tel: +81 (0)3 3861 8231
Fax: +81 (0)3 3861 8259 - Email: info-sci.jp@horiba.com
Germany: HORIBA Jobin Yvon GmbH, Hauptstrasse 1, 82008 Unterhaching - Tel: +49 (0)89 46 23 17-0 - Fax: +49 (0)89 46 23 17-99 - Email: info-sci.de@horiba.com
Italy: HORIBA Jobin Yvon Srl, Via Cesare Pavese 35/AB, 20090 Opera (Milano) - Tel: +39 0 2 57 60 30 50 - Fax: +39 0 2 57 60 08 76 - Email: info-sci.it@horiba.com
UK: HORIBA Jobin Yvon Ltd, 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ - Tel: +44 (0)20 8204 8142 - Fax: +44 (0)20 8204 6142 - Email: info-sci.uk@horiba.com
China: HORIBA Jobin Yvon SAS, Room 1801, Capital Tower No.6, Jianguomenwai Av., Chaoyang District, Beijing 100022 - Tel: +86 (0)10 8567 9966 - Fax: +86 (0)10 8567 9066
Email: info-sci.cn@horiba.com
Other Countries: Tel: +33 (0)1 64 54 13 00 - Email: info.sci@horiba.com