Application Note

Evaluation, Control and Diagnosis of an ICP Through Simple Experiments

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Keywords: general

1 Introduction

To undertake an analysis, one must go through a long chain of processes from sampling to reporting of the results. To obtain reliable results, the chemist must ensure that none of these steps introduces a systematic error. To do this, checks must be made on each process. In the case of ICP, it is necessary to check, by means of a set of tests, that the instrument provides the initial analytical performance used as a comparison basis. The set of tests provide:

1) Checks on the main components of the ICP,
2) Diagnosis of any malfunctions,
3) Checks on analytical performance.
More particularly, the following parameters are checked: repeatability and reproducibility, accuracy, absence of drift (long term stability), selectivity (practical resolution of the dispersion system), absence of matrix effects or inter-element effects and detection limits.

Highly sophisticated diagnostic tests have been developed and described in the literature for understanding the role of the plasma and the effects of the operating parameters. The understanding of ICPs have been considerably improved by these experiments, but it is difficult to implement them on commercially available ICP systems. It is therefore necessary to provide simple experiments that can be applied more widely. This motivated the development of a set of tests based on previous work on drift [1], on the measurement of the practical resolution [2], on diagnosis using the ratio of the intensity of an ionic to that of an atomic line [3], and on a scale of detection limits [4].

If you would like more information on this subject, you can read the publication *"Simple experiments for the control, the evaluation and the diagnosis of inductively coupled plasma sequential systems",* E. Poussel, J.M. Mermet, O. Samuel-Hirsch, Spectrochimica Acta, 48B, 743-755 (1993) and also you can obtain document A0037/1/E from HORIBA Scientifc.

2 Effect of ICP components on analytical performance

An ICP consists of the following main components: an RF generator, an inductor to generate the plasma, a torch to confine the discharge, a sample injection system (nebulizer, spray chamber and injector), a collimator, a dispersion system and a detector. Each component can have an effect on the analytical characteristics (Table 1).

Table 1: Effect of component on analytical characteristics

	Generator	Optics		
		Nebulization		Detection
Repeatability	*	*	*	*
Accuracy		*		
Stability	*	*	*	
Interferences	*	*		
Selectivity			*	
Limits of detection	*	*	*	*

Repeatability can be degraded by lack of stability of the RF generator matching unit; by fluctuations in the transport of the aerosol or the drain, insufficient integration time favoring shot noise, or by the photomultiplier tube noise caused by inadequate bandwidth of the dispersion system.

Reproducibility can be affected by the replacement of one of the components, in particular replacement of the torch. A lack of long-term stability, indicated by drift, may be caused by a change in the applied power, or in the gas flow rates. Other causes include partial clogging of the nebulizer, a change in the temperature of the spray chamber and a deposit on the injector tube. The dispersion system may also contribute to drift by contamination of the collimation system (lens or mirror, possibly optical fibers) and a change in the focusing and wavelength positioning conditions.

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It has been shown that matrix effects are minimized by using a high generator power (>1.2 kW) and a long sample dwell time. The latter is obtained by using aerosol gas flowrates below 1 L/min. It is therefore important to check the power and the gas flow rates.

Good **selectivity** is essentially related to the practical resolution of the dispersion system, which can be degraded by a change in the position of an optical component (for example caused by vibrations).

Good **detection limits** can be obtained only if each constituent part of the ICP system is operating under ideal conditions. The detection limit is known to depend on the relative standard deviation of the fluctuations in the background and on the signal-to-background ratio as well as the optics. The latter is related to the effectiveness of the nebulizer and to the bandwidth of the system. The relative standard deviation depends on the shot noise (minimized by longer integration time and smaller bandwidth) and on the flicker noise (RF generator and sample injection system). The detection limits must therefore be checked after ensuring that each part satisfies specified criteria.

3 Elements and tests

In addition to naturally available argon, a limited number of elements are used in the set of tests: Ba (5 mg/L), Mg (5 mg/L) and Zn (5 mg/L). The lines used and the energies are given in Table 2

Table 2: Excitation Energy (E_{exc}), Ionization Energy (E_{ion}), and the sum of these two energies (E_{sum}) for different lines used in this diagnosis

Elements	E_{exc} (eV)	E_{ion}(eV)	E_{sum}(eV)
Ar I 404 nm	14.69		14.69
Ba II 455 nm	2.72	5.21	7.93
Ba II 233 nm	6.01	5.21	11.22
Mg I 285 nm	4.35		4.35
Mg II 280 nm	4.42	7.65	12.07
Zn II 206 nm	6.01	9.39	15.40

Although the number of lines in Table 2 is limited, a large amount of information can be obtained, by considering the line width, the absolute intensity, the ratio of the intensities of a pair of ionic and atomic lines, and the relative standard deviation of the intensity. The use made of the lines is summarized in Table 3.

Table 3: Use of the test elements for the evaluation and the diagnosis of the ICP system

Line and Test	Measurement	Component
Ba II 233 nm: profile	UV resolution	Dispersive system
Ba II 455 nm: profile	Vis resolution	Dispersive system
Mg II 280/ Mg I 285	Energy transfer	Generator
Background 455/Background 233 nm	Lens/mirror contamination	Collimator
Mg I 285 nm/ adjacent background	Nebulizer effectiveness	Nebulizer
RSD Mg I 285 nm	Nebulizer repeatability	Nebulizer
RSD Mg I 285 nm	Reproducibility	ICP system
Ba II 233 nm	Detection limit	ICP system
Zn II 206 nm	Detection limit	ICP system
RSD Ar I 404 nm	Drift	ICP system
RSD Zn II 206 nm	Drift	ICP system
RSD Ba II 455 nm	Drift	ICP system

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4 Flow chart of the procedure

The experiment described in the previous section must be performed according to a given sequence (shown in Figure 1). The first step is to verify the practical resolution of the optical system, as this measurement is independent of the RF generator efficiency and the sample introduction system. The second step is to verify that the transfer of energy is adequate by using the line intensity ratio of Mg II to Mg I. If this ratio is good, one can compare the 455/233 signal intensity ratio, and if the value is higher, this could signify that there is absorption of light. The following step is to check the nebulizer by measuring the SBR of the Mg I 285 line. If the excitation conditions are constant as previously checked, the SBR of the Mg I line depends mainly on the efficiency of the nebulizer. Subsequently, the stability of the sample introduction system is assessed through the value of the RSD. Finally, the limits of detection of Ba II 455 nm and Zn II 206 nm are measured and compared to previous values. A drift test can be carried out by the use of the Ba II 455 nm and Zn II 206 nm lines.

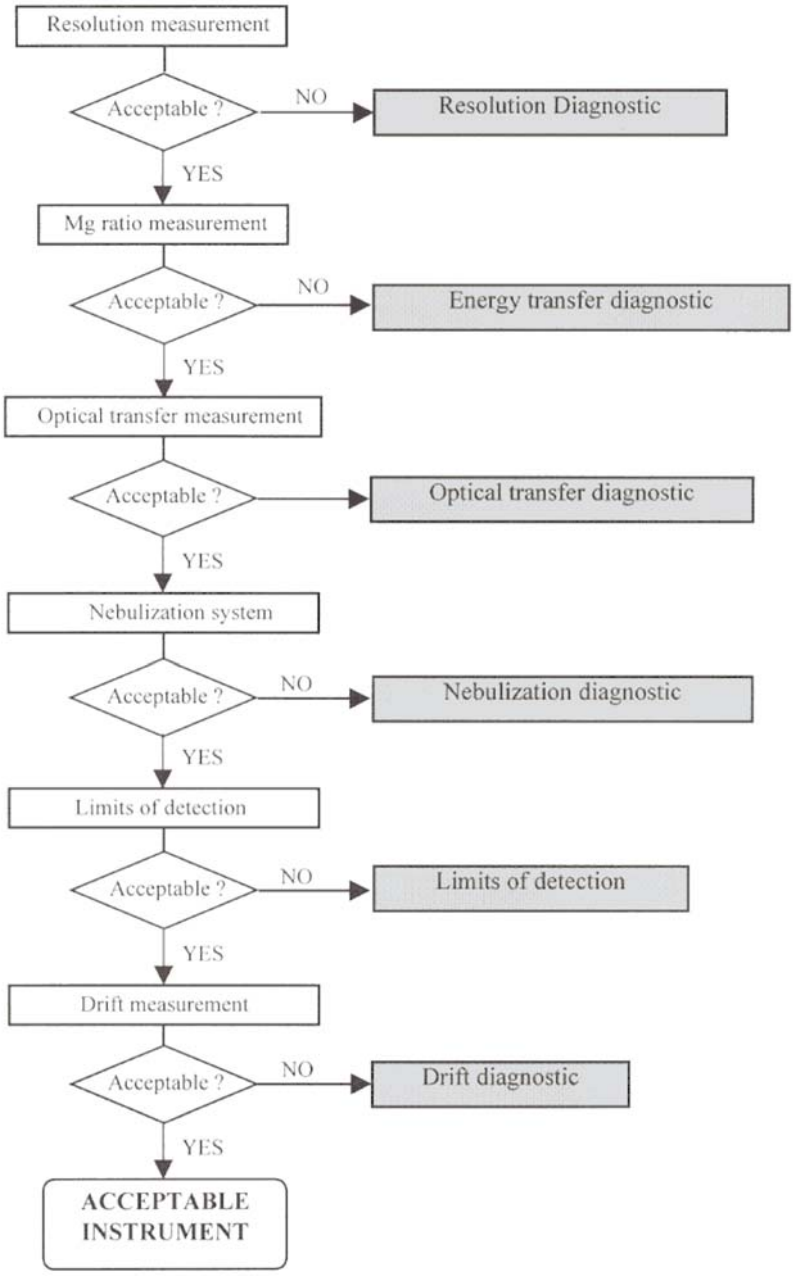

Figure 1: Flow chart of the procedure used for the evaluation and the diagnosis of an ICP system

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5 Example of long term diagnosis

Results shown in Table 4 represent data from a JY 24/124 instrument. This instrument is used for a variety of matrices, including cement, bitumen, and wastewater. This leads to numerous changes of the sample introduction system. One can see that the RSD over 6 months are very good, except for the sample introduction system, because nebulizer clogging occurred causing the nebulizer to be changed twice.

Table 4: Example 1

	Duration	Mean value	Sigma	RSD(%)
Energy transfer	6 months	10.5	0.37	3.5
Optics transfer	6 months	9.3	0.4	4.3
Nebulizer efficiency	2.5 months	124	6.4	5.2
Repeatability	6 months	0.8		
Reproducibility	2.5 months	2308	182	7.9
Zn Limit of detection	2.5 months	1.2	0.55	

Table 5 represnt data from a JY38/138/238/ULTIMA instrument. The matrices analyzed on this instrument are various types of wastewater and oil. The results show very good performance over more than one year.

Table 5: Example 2

	Duration	Mean value	Sigma	RSD(%)
Energy transfer	13 months	9.3	0.68	7.3
Optics transfer	13 months	0.98	0.26	
Nebulizer efficiency	4 months	487	11.7	2.4
Repeatability	13 months	0.5 %		
Reproducibility	4 months	1108	58	5.2

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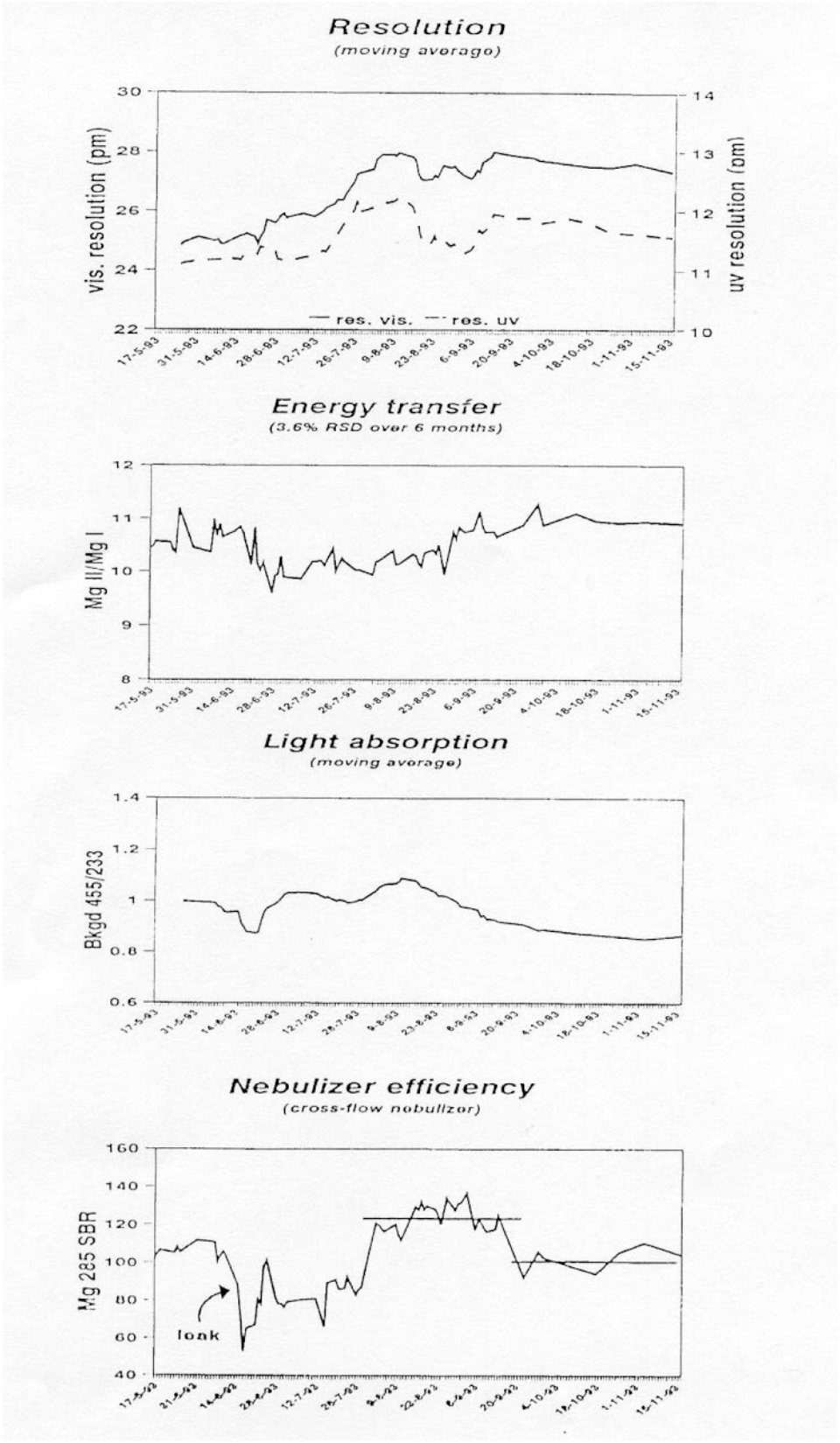

Figure 2: Resolution, energy transfer, light absorption, and efficiency curves

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6 Example of a malfunction in the instrument

This example illustrates the detection of a degradation in the energy transfer of the JY138 ICP system based on the use of the Mg II/Mg I line intensity ratio. The ratio is shown over a period of two months. During the first month of the experiment, a decrease in the ratio was observed which clearly indicated a change in either the power or the energy transfer. In fact, the system had a blockage in the recirculating water cooling system of the load coil. The system was cleaned with acidified water, then with deionized water. Unfortunately, some acidified water remained in the circuit causing the dissolution of copper from the coil. Because of the increase in the conductivity of water, some power was therefore dissipated into the water instead of being transferred into plasma. Once the origin of this problem was found, the circuit was carefully cleaned, resulting in a two-fold improvement in the intensity ratio. Then, over a period of more than one month, regular checks indicated no significant change in the ratio.

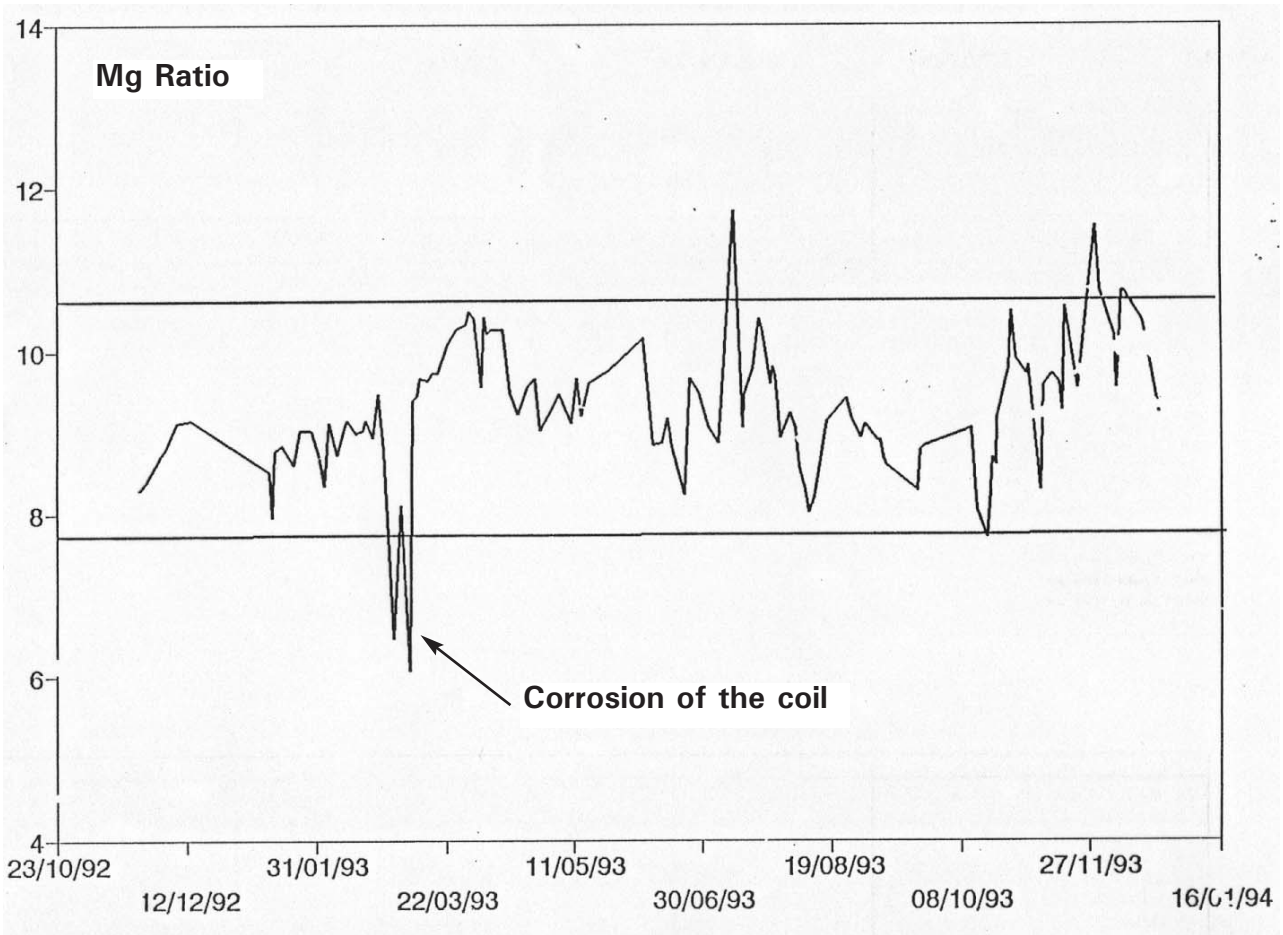

Figure 3: Example of malfunction

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7 Conclusion

Previously sophisticated diagnostics could only be carried out in research laboratories. Now, however, it is possible to perform some simple experiments in order to control and evaluate an ICP system and to identify problems. Among these tests, the one using the ratio of the Mg lines is the most critical, as many parameters can affect it.

The experiments described are fast and easy to conduct and can be stored as a standard analytical method and can provide some explanation about the origin of a degradation of the analytical performance. To obtain a ratio that remains constant to within a few percent over a period of several weeks or months requires rigorous maintenance of the instrument (replacement of a component, adjustment of operating parameters) but this will provide high reproducibility of analytical performance.

These experiments can also be easily adapted to set up control charts, once the accepted values of the line intensities and ratios and their fluctuations have been determined.

8 References

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