

# Analysis Procedure for Elemental Analysis of Water Samples by Spectroil M Instrument

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## Abstract

Elemental Analysis in water samples is essential to determine the water quality, the concentration of each elements varies according to water source and nature, for example, seawater considered rich with chloride and other monovalent and Divalent cations such as Sodium, Calcium, Magnesium and Potassium with traces of Boron and barium ions, with total dissolved solids range from 44,000-60,000 mg/l, while formation water (produced water) at oil field has the same ions however with higher concentration due to high Total dissolved Solids which is in range of 100,000-300,000 mg/l. on the other hand, drinking water has very low concentration from the same cations in very small concentration compared with sweater and oil field formation water. The common instrument used for elemental analysis for high and low-level concentrations up to part per billion (ppb) is ICP-OES (Inductively coupled Plasma Optical Emission Spectroscopy). Despite ICP-OES is the best choice for elemental analysis, it has associated cost to operate such as ultra-pure Argon gas, specific sample introduction system for each sample matrix such as Torch, Spray Chamber, Nebulizer and plastic tubing which is different in shape and diameter according to the sample type, in the present paper we proved that Spectroil M instrument which is a compact, rugged and easy to use optical spectrometer designed specifically for wear particle analysis, contaminants and additives in lubricants, hydraulic fluids and coolants can be utilized for water analysis as well. We have established a novel analytical method to be able to determine 16 dissolved metals in water based samples which are (Cu, Fe, Na, Ca, Mg, Pb, Mn, Al, Ag, Cd, B, Ba, K, Cr, Ni and Zn), the instrument is capable to detect the dissolved elements in waste water and produced water samples in the range from 200 ppb up to 10% With lower cost and high accuracy, the instrument is calibrated with three reference standards (0, 100 & 900 mg/l) using the instrument built-in software instructions. Then the sample can be easily analyzed by introducing 1.5 ml in disposable plastic cup. The procedure has been validated against traditional technique of ICP-OES (AVIO-200 Perkin Elmer model). Hence, this application which uses the rotating disc electrode (RDE) technique provides a quicker, easier and cheaper backup/alternative to the use of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) technique.

**Key Words:** Spectroil M • Elemental analysis in water • Spectroscopy • Dissolved metals • ICP-OES

## Introduction

Determining the chemical composition of oils has been measured using Spectroil Q100, which is a completely solid-state spectrometer, specifically designed for the analysis of oil samples. With this spectrometer it can be measured trace levels of elements dissolved or deposited as fine particles in mineral or synthetic oil-based products using long established and reliable technique with rotating disk electrode. The device meets the requirements of ASTM D6595 standard method for the determination of wear metals and contaminants in used lubricating oils and hydraulic mixtures. Increase metals content and decrease additives content have been modelled using linear function as in publication [1].

### How ICP-OES analyze a fluid sample to determine sub-ppm level elements?

ICP-OES is a powerful, versatile, and advanced analytical technique with excellent detection properties. Due to its extraordinary features, it has been

widely employed for the analysis of a wide variety of chemical elements in the past few years with great success. It offers the least detection time, lower detection limits, broader linear dynamic range, and greater matrix tolerability as well as negligible chemical interferences. Beyond this, it can handle multiple varieties of samples including aqueous, inorganic, organic liquids, and solids as well. It comprises complex instrumental makeup which enables it to detect up to 2 to 70 elements simultaneously with great accuracy. Recent reports evidenced that this hyphenated technique has been employed in several analytical determinations including food analysis, agricultural investigations, geological studies, drug/metabolite analysis, and environmental and forensic sciences. In the present compilation, a detailed description of the fundamental principles of ICP-OES has been provided along with its various sophisticated functional components. Also, the reported applications of this technique in different fields have been discussed highlighting the basic experimental setups and outcomes by presenting the data as tables. This summarization may be helpful to analysts to get insights into the working as well as performance characteristics of this technique [2].

### ICP-OES: analysis of fluid samples to determine sub-ppm level elements

Inductively coupled plasma (ICP) has become the dominant source for rapid spectroscopic multielement analysis as a result of a set of "legendary" attributes, including low detection limits, a wide linear dynamic range, and high precision [3].

### Success of the ICP technique

To evaluate the remaining problems and their possible origins is useful to consider some of the ICP's desirable characteristics, including the following. Intense emission is produced from many different spectral lines for almost all elements. Compared with flames or graphite furnaces, the ICP is much

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more highly excited. Temperatures measured in Argon ICPs range from 5000 to 9000 K (Kelvin), depending on experimental conditions (power, gas flow rates, and sample transport rate), where in the plasma the measurement is made, and how the temperature is measured. Emission intensities depend on the number of ions (atoms) in the volume from which the signal is collected and the fraction of ions (atoms) that are in an excited state. The population of a particular excited state is proportional to the Boltzmann factor,  $e^{-E/kT}$ , where E is the energy of the upper state of the spectroscopic transition (usually between 3 and 7 eV for the most sensitive lines emitted by the ICP), k is the Boltzmann constant, and T is temperature [4].

### Advantages of arc spark optical emission spectrometry

Optical emission spectrometry involving an electrical discharge generated across two electrodes has several advantages over other similar techniques. The instrumental procedure has extremely high sensitivity for a wide range of trace elements (down to ppm detection limits for many); it possesses simultaneous multi-element analysis capability and has extremely rapid analysis times (one sample every 3-4 minutes [5]).

Despite ICP-OES is the best choice for elemental analysis, it has associated cost such as (ultra-pure Argon gas, specific sample introduction system for each sample matrix such as Torch, Spray Chamber, Nebulizer and plastic tubing which is different in shape and diameter according to the sample type). Therefore, to overcome the disadvantages of ICP-OES technique, in this paper, we have created a new calibration and testing procedure to be able to analyse dissolved and dispersed elements in different water types by Spectroil M instrument, which is not part of the instrument known applications, to be utilized as an alternative technique for elemental analysis for water and waste water instead of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

## Methodology

### Elemental analysis by Spectroil M instrument

- Spectroil M (Oil and Fuel Spectrometer)
- Graphite Rod and Disc Electrodes
- Sample Cups (1.5 ml capacity)

### Elemental analysis by ICP-OES (for results validation)

- AVIO 200 Perkin Elmer ICP (Inductively Coupled Plasma Optical Emission Spectroscopy)
- Ultra-Pure Liquid Argon Tank (for Plasma Generation) with 100 psi stable flow
- Air Compressor with Drier as a shear gas to prevent plasma tailing
- Auto-sampler

### Glassware

- 100 ml Volumetric Flask
- 1000 ml Volumetric Flask
- 0.1-1 ml of Adjustable pipette
- 1-10 ml adjustable pipette

Note: All glassware and pipettes were calibrated by certified calibration laboratories according to ISO-IEC 17025-2017 requirements.

### Reagents

- Certified Reference material for multi element standard from MERCK
- Free metals concentrated Nitric Acid
- De-ionized water according to ASTM type II

## Spectroil M description and methodology

**How Spectroil M analyzes a fluid sample to determine sub-ppm level elements:** Spectroil M RDE-OES consists of three main components. These components are:

**Excitation source:** introduces energy to the sample. This includes a high voltage AC source that applies voltage across a small gap formed by a purified graphite rod and disc, with the disc rotating and picking up oil from the sample holder under it.

**Optical system:** separates and resolves the resulting emission from that excitation into its component wavelengths.

**Readout system:** detects and measures the light that has been separated into its component wavelengths by the optical system and presents this information to the operator in a usable fashion.

A specific calibration program is applied to raw spectrum which eliminates the matrix effect [6].

Figure 1 shows the configuration of Spectroil M instrument.

### Benefits of utilizing Spectroil M instrument rather than ICP-OES

Although the most common traditional method to determine the metals in water samples is ICP-OES & ICP-MS, it requires several accessories that include glass parts (Torch, Spray Chamber and nebulizer). These parts are subject to frequent breakdown and replacement.

Each type of water (drinking water, wastewater and saline water) require special analytical sets (Torch, Spray Chamber and Nebulizer).

High purity Argon gas is required, which is essential to conduct the analysis.

In the case of lube oil sample analysis using ICP-OES, a special sample introduction system has to be added to avoid interference, however by applying this paper's procedure; Spectroil M can conduct the analysis for oil and water samples without any additional special parts required.

## Results and Discussion

Initially the instrument was calibrated using a certified reference material and the calibration was conducted according to the instrument's software instruction, however the results interpretation was conducted externally by plotting the calibration curves in separate excel sheets based on the output intensities from the instrument's software. Intermediate checks with different has been checked by both calibrations data (by the instrument and the external calculation sheet). The results were matched by applying the calibration curve equation for each calibration curve.

### Standards preparation

Several standards were prepared from 10,000 mg/l multi element certified reference standard (Cu, Fe, Na, Ca, Mg, Pb, Mn, Al, Ag, Cd, B, Ba, K, Cr, Ni and Zn). A blank was prepared from ultra-pure water which was generated through a Millipore Distillation Unit with 1% of metals-free nitric acid, 100 mg/l was prepared by transferring 1 ml from the 10,000 mg/l multi element standard into calibrated 100 ml volumetric flask and made up with ultra-pure de-ionized water. The last standard (900 mg/l) was prepared by transferring 9 ml from the 10,000 mg/l multi element standard into a calibrated 100 ml volumetric flask and made up with ultra-pure de-ionized water.

### Calibration procedure

An automated autosampler capable of analyzing 45 samples was utilized during the calibration and sample analysis. Three standards (0, 100 and 900 ppm) with 6 replicates (6 different sample cups with 1.5 ml capacity) were run by Utilizing OilM Windows® software and following the calibration and profiling steps to establish the calibration curve. The instrument software was configured to analyze each standard 6 times and after the six replicates were

run, all readings were reviewed on the analysis screen and any outlier values that did not meet the required minimum deviation from the true value were rejected to avoid a non-linear calibration curve. The average values of the recorded intensities were used to establish the calibration curve.

### Standardization check

The prepared standards were run as unknown samples and a verification of the results was done to ensure that they were within 90% of the true value. If the variation of the results is more than 10%, then the instrument has to be recalibrated with freshly prepared standards.

The charts (Figures 2-4) show the calibration curves for 16 elements in water matrix with different concentrations. The output calibration for 5 elements (Manganese, Vanadium, Chromium, Zinc and Copper) showed linearity up to 100 ppm with its equation that was utilized for determining the concentration of

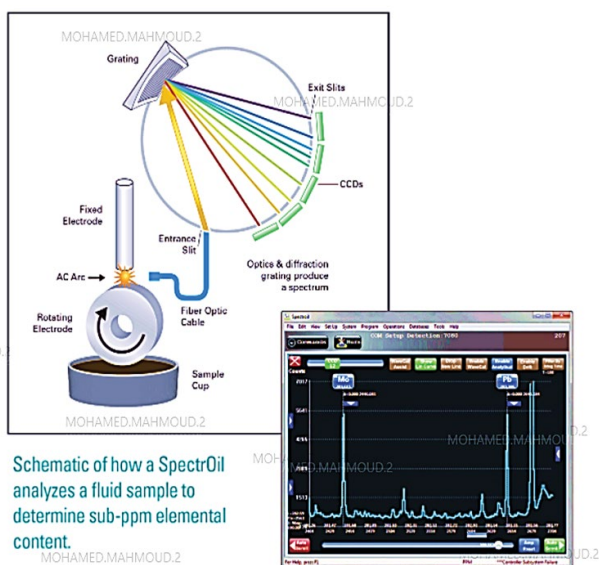


Figure 1. Spectroil RDE-OES analysis.

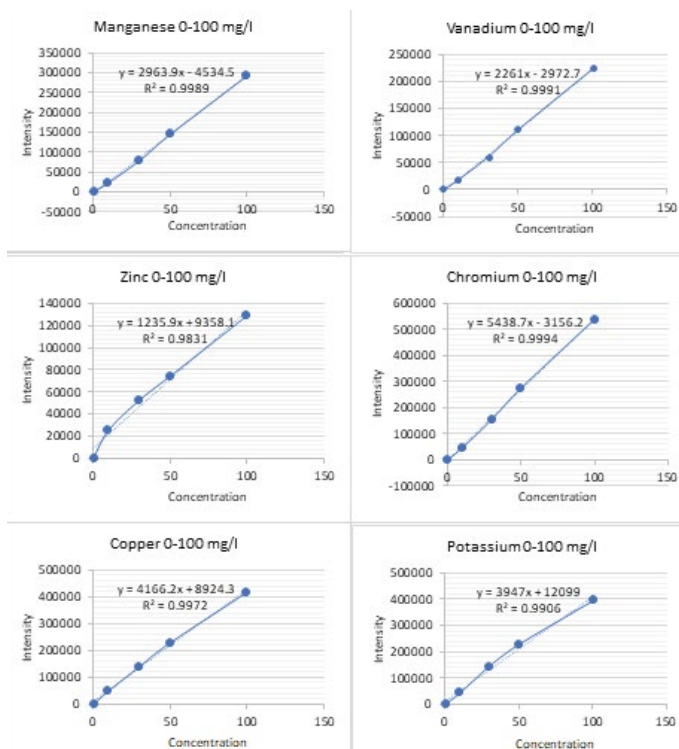


Figure 2. Output calibration for 5 elements (Manganese, Vanadium, Chromium, Zinc and Copper) 0-100 ppm.

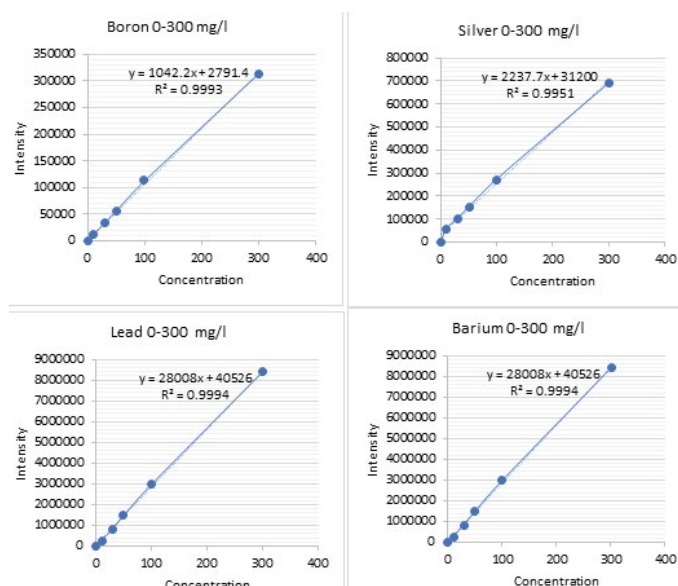


Figure 3. Calibration curve for 5 elements (Lead, Barium, Boron and Silver) 0-300 ppm.

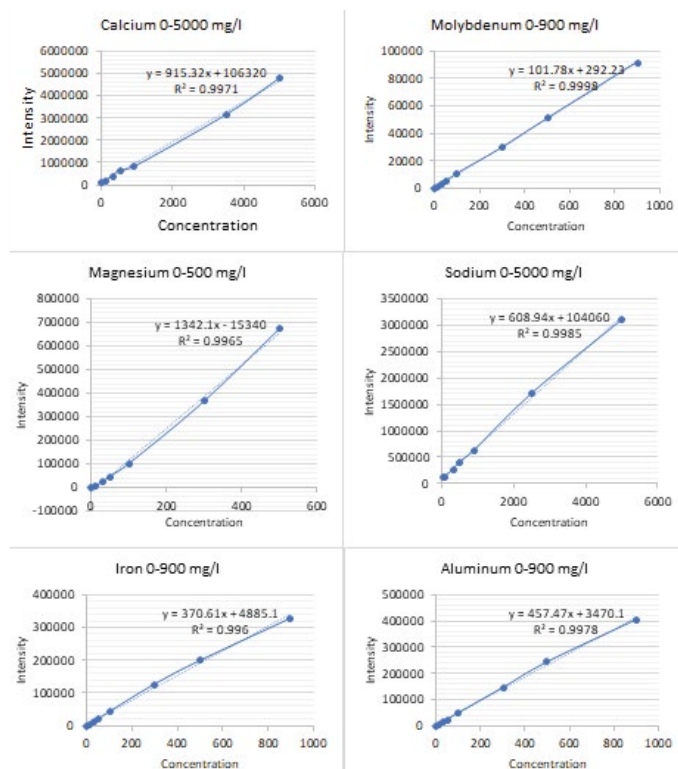


Figure 4. Calibration curve for Sodium, Aluminum, Iron, Molybdenum, Calcium, Magnesium and Cadmium.

the unknown samples in Figure 2, while Figure 3 shows the calibration curve for 5 elements (Lead, Barium, Boron and Silver) with calibration range from 0-300 ppm.

Sodium, Aluminum, Iron, Molybdenum, Magnesium and Cadmium showed linear calibration curve at higher concentration from 500 up to 5000 mg/l as shown in Figure 4.

### Method validation

Several samples and standards with known concentration been analyzed by using Spectroil M instrument as well as by AVIO 200 Perkin Elmer ICP-OES, the output results were within the accepted range by maximum 10% variation as shown in the Tables 1 and 2.

Both Tables 1 and 2 shows the accuracy of elements concentrations

**Table 1.** Method Validation for Spectroil M with AVIO 200 ICP-OES for 1.0 mg/l Standard.

Metals	Theoretical Concentration (mg/l)	Spectroil-M Instrument Results (mg/l)	AVIO 200 ICP-OES (mg/l)	Difference (mg/l)
Fe*	1.0	1.1	1.02	0.08
Cr	1.0	1.10	1.03	0.07
Pb	1.0	1.08	0.99	0.09
Cu	1.0	1.09	0.99	0.1
Al*	1.0	1.27	1.20	0.07
Ni	1.0	1.27	1.02	0.25
Ag	1.0	1.08	1.03	0.05
B	1.0	0.82	0.99	0.02
Na	1.0	1.13	0.99	0.14
Mg	1.0	1.11	1.02	0.09
Ca	1.0	1.04	1.02	0.02
Ba	1.0	1.02	1.00	0.02
Zn	1.0	1.12	1.03	0.06
K	1.0	1.03	0.98	0.05
Cd	1.0	0.99	1.02	0.03
Mn	1.0	1.39	1.03	0.04

**Table 2.** Method Validation for Spectroil M with AVIO 200 ICP-OES for 200 mg/l Standard.

Metals	Theoretical Concentration (mg/l)	Spectroil-M Instrument Results (mg/l)	AVIO 200 ICP-OES (mg/l)	Difference (mg/l)
Fe	200	211	195	8.0
Cr	200	216	203	6.5
Pb	200	202	208	3.0
Cu	200	205	195	5.0
Al	200	211	210	0.5
Ni	200	215	206	4.5
Ag	200	200	194	3.0
B	200	201	203	1.0
Na	200	210	196	7.0
Mg	200	208	203	2.5
Ca	200	205	210	2.5
Ba	200	203	199	2.0
Zn	200	201	207	3.0
Mn	200	209	203	3.0
K	200	202	197	2.5
Cd	200	197	201	2.0

by Spectroil M instrument compared with the most common analyzer for elemental analysis for water samples (ICP-OES) at low and high concentration for all the elements.

### Advantages of this new test method

Performing elemental analysis using the procedure outlined in this study,

in different types of water samples, utilizing the Spectroil M instrument has many advantages and eliminates the associated costs with the other traditional techniques such as:

- No carrier gases required, no special sample introduction system such as Torch, Nebulizer and Spray Chamber which are required by ICP-OES.
- The required sample volume is minimal (approximately 1.5 ml).
- No dilution is required for the samples with high TDS values up to 20%.

## Conclusion

From the above results and discussion, it can be concluded that, by following the explained procedure for calibration of the instrument, the desired accurate results can be obtained either directly from the instrument or by utilizing external calibration curves for several concentrations, in addition to the specified concentrations configured with the instrument software. The results variance obtained fall within the 95% confidence level.

The Spectroil M RDE-OES instrument can be utilized as an alternative technique for elemental analysis in different types of water samples such as:

- Produced water for geochemical properties which contain high dissolved solids in the range of 10-20%, with high concentrations of Sodium, Calcium, Magnesium and Potassium, without the need for sample dilution, whereas this cannot be done using ICP-OES without dilution.
- The detection limits of some heavy metals can reach up to 50 ppb for drinking and waste water samples.

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