Jobin Yvon and Optical Emission Spectroscopy

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Abstract

While many know that Jobin Yvon's (JY's) involvement in optics can be traced to its origin in 1819, few are aware of the company's early efforts in the development of optical emission spectroscopy (OES). The company's expertise in optics led to the wide range of successful products that are made today by the Emission Division such as Inductively Coupled Plasma, Spark Emission and Glow Discharge Spectrometers. In this paper, we will introduce emission spectroscopy and review JY's contribution to this important branch of elemental analysis.

1 Introduction

It is generally agreed the scientists Kirchoff and Bunsen conducted the first experiments in emission spectroscopy in 1859. The latter is best remembered for a burner of the same name. In 1859 Bunsen wrote a colleague:

> *Kirchoff has made a wonderful, entirely unexpected discovery in finding the cause of the dark lines in the solar spectrum...thus a means has been found to determine the composition of the sun and fixed stars with the same accuracy as we determine sulfuric acid, chlorine, etc., with our chemical reagents. Substances on the earth can be determined by this method just as easily as on the sun, so that, for example, I have been able to detect lithium in twenty grams of sea water.*

The two would later discover the elements cesium and rubidium using the spectroscope in Fig.1 (from *Annalen der Physik* (1860)). Light from salts introduced (E) into Bunsen's burner (D) was dispersed by a prism (F) and the resulting spectrum was visually observed by a telescope (C) by moving the prism. We see this dispersive effect on light in a rainbow where water droplets refract the sun's light into a visible spectrum across the sky. Through their spectroscope Kirchoff and Bunsen found that each element emitted light at specific wavelengths, which could be used to not only discover new elements, but also determine their presence and concentration.

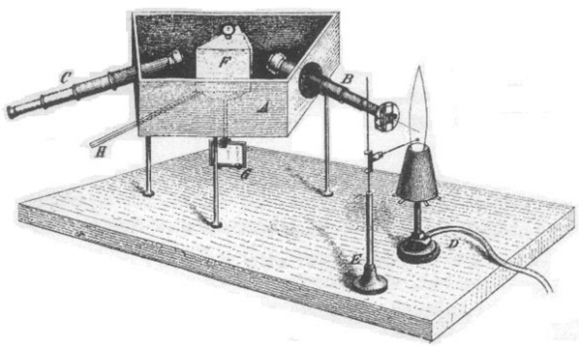


Fig.1 The Spectroscope Used by Kirchoff and Bunsen

2 Jobin Yvon

Amédée Jobin acquired the company founded in 1819 by the celebrated French optician Jean-Baptiste Soleil from Léon Laurent. Laurent designed a famous polarimeter that is named after him. After the 1893 acquisition, Jobin was involved in the design and manufacture of optical instruments for a number of clients including C. Fabry for whom he constructed the renowned Fabry-Pérot interferometer in 1899.

One of the first spectrographs Jobin's company made that we are aware of is shown in Fig.2. Here the photographic plate replaced the telescope of Kirchoff and Bunsen's spectroscope. One of these instruments may have been used on board one of the research vessels of Prince Albert I of Monaco, which is most interesting, as we will see later.

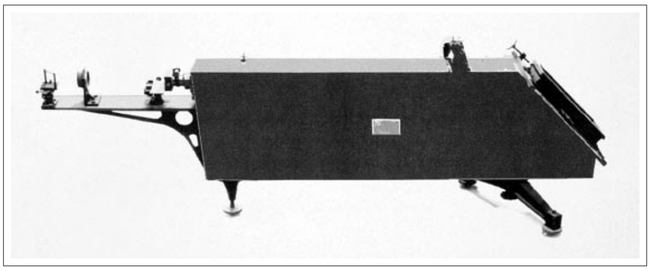


Fig.2 Quartz Spectrograph

"Quartz spectrograph, meant to photographically measure the spectrum of various materials under analysis.
This instrument was constructed by the Paris firm of Jobin and Yvon in 1901. Several of these instruments were made by the engineer Amedee Jobin." (Photo and description from the U.S. National Oceanic & Atmospheric Administration (NOAA) Central Library. Photo courtesy of the Oceanographic Museum of Monaco.)[*1]

[*1] Direct quote from the NOAA photo gallery

After the photo from 1901, we have little information on the company's further involvement in emission spectroscopy, although it is certain that its optics continued to be used in emission instrumentation. In 1962, the company began to rule diffraction gratings after it moved into its new facility in Longjumeau, which still serves as the factory for JY's Emission Division. Shortly thereafter, in 1968, JY introduced the first commercially available holographic gratings. This was at the time that the technique of inductively coupled plasma spectroscopy (ICP) was being developed, which was a fortunate coincidence of events.

3 Inductively Coupled Plasma-Optical Emission Spectroscopy

3.1 Principle of ICP-OES

An ICP employs an argon plasma to excite atoms with a temperature at least 7,000 °C higher than the burner of Bunsen. This allows the excitation of some 75 elements in the periodic chart by nebulizing a fine mist of a liquid sample into the hot plasma. It also generates very complex spectra that require much better resolution and light gathering power, i.e., a larger aperture, than the optical systems of the day. These were primarily polychromator systems where an array of photo-detectors on a focal curve was used to resolve the less challenging spectra generated by an arc or spark in order to measure the elements.

Due to the increased optical requirements, JY used its existing optical technology as the basis of a new ICP introduced in 1977. The THR 1000 one-meter focal length monochromator became the heart of the famous JY 38, which was the first computerized, sequential ICP spectrometer. Its resolution, low stray light and freedom from optical aberrations that evolve from the use of a holographic grating made it an immediate success. This also marked the start of the JY Emission Division.

This same monochromator, with numerous refinements over the years, is now used in the ULTIMA 2 (Fig.3), which was jointly developed with Horiba and is the first A-design 21[*2] designed product of Horiba.

[*2] Project name to unify the design of HORIBA Group

Fig.3 ICP Optical Emission Spectrometer ULTIMA 2

It is because of the excellence of the optics of the ULTIMA 2 that it offers today's analyst the best detection limits and the fewest interferences for trace level (parts per billion) analysis. In addition to the ULTIMA 2, JY makes several modular combination ICP systems that incorporate a "simultaneous" polychromator in addition to the sequential monochromator.

The polychromator (0.5 or 1.0 m focal length) may have as many as forty or more photomultiplier detectors that are viewing the plasma. These systems allow more elements to be determined in a given time and the polychromator may improve the precision of the data for higher concentrations of an element, while the monochromator provides greater resolution and better sensitivity for challenging elements at the trace or ultra-trace level.

All the ICP models have a range of options and accessories to cover a multitude of applications. In addition there are systems that have been designed specifically for a particular application. These "made-to-measure" instruments are in use in nuclear glove boxes and laminar flow hoods, in a mobile lab for the US-EPA, and in edible oil plants, which require a system, that keeps the sample hot and liquid up to 80 °C. Most interesting is that a custom JY ICP is currently in use aboard the *JOIDES Resolution* ocean drilling ship over 100 years since JY made a spectrograph for the oceanographic research of Prince Albert I. This instrument may be viewed at www.oceandrilling.org under Facilities/Labs.

3.2 Application of ICP-OES for Dialysis Solution Analysis in the Medical Field

3.2.1 Introduction and Standardization

Dialysis is used for blood purification in the treatment of renal failure. ICP-OES is particularly suitable to measure the solutions used in the dialysis procedure for the high accuracy analysis of Na, K, Ca, Mg and Cl. These element's role as the electrolytes in the solution requires that their concentration be determined with great accuracy.

Two dialysis samples were analyzed, labeled S1 and S2. These samples contain K, Ca, and Mg in the chloride form. In sample S1, Na is present as a mixture of chloride and acetate. It is at a total concentration of 140 mmol/L, with the acetate compound concentration of 35 mmol/L. In S2, the Na is present as the chloride and is at a concentration of 102 mmol/L.

As the level of acetate is considered negligible, a solution of 6 g/L NaCl (105 mmol/L) was prepared to matrix match the standards. Four standards for K, Ca and Mg were prepared with 250 mL of the Na solution using 1,000 mg/L Spex Standards. Four standards were also prepared for Na and Cl at concentrations of 5, 6, 7 and 8.2 g/L of NaCl.

3.2.2 Analysis

Two series of analyses were made. The first was a direct analysis, without dilution, and the second was with a 1:10 dilution with deionized water.

The operating conditions are listed in the Table 1.

Table 1 Operating Conditions

Parameter	No dilution	With dilution
Generator power	1400 W	1400 W
Plasma gas flowrate	13 L/min	13 L/min
Auxiliary gas flowrate	0.40 L/min	0 L/min
Sheath gas flowrate	0.35 L/min	0.2 L/min
Nebulizer gas flowrate	0.67 L/min	0.67 L/min
Nebulizer flowrate	2.8 bars	2.8 bars
Sample uptake	1 mL/min	1 mL/min
Type of nebulizer	Concentric	Concentric
Type of spray chamber	Cyclonic	Cyclonic
Argon humidifier	Yes	Yes
Injector tube diameter	3.0 mm	3.0 mm

The line with the highest sensitivity was used for analysis of each element (Table 2), as there were no problems with interferences. The analysis conditions were the same for all elements (Table 3).

Table 2 Analysis Line

Element	Wavelength (nm)	Background correction point (nm)
Ca	317.933	0.0325
Cl	725.665	0.0233
K	769.898	0.0372
Mg	279.806	0.0349
Na	588.995	0.0381

Table 3 Analysis Conditions

Element	Slits(μm)	Analysis mode	Integration time(sec)
All elements	20×15	Gaussian	2

The expected concentrations of the two samples are presented in Table 4.

Table 4 Expected Concentrations

Expected concentrations for Sample S1:

	Minimum	Expected	Maximum.
Ca	66.53	70.14	73.75
Cl	3799.54	3993.27	4187.00
K	74.29	78.2	82.11
Mg	23.09	24.31	25.52
Na	3138.1	3218.6	3299.1

Expected Concentrations for Sample S2:

	Minimum	Expected	Maximum.
Ca	66.53	70.14	73.75
Cl	3688.0	3882.10	4076.2
K	74.29	78.20	82.11
Mg	23.09	24.31	25.52
Na	2286.4	2345.0	2403.6

The two samples were measured three times each with three replicates for each measurement, both directly and with a dilution of 1:10. The results are presented in Table 5, with the concentrations given in mg/L and the RSD in %.

Table 5 Results of Analysis

Results for Sample S1, no dilution:

Element	Measurement 1		Measurement 2		Measurement 3		Mean conc.	RSD (%)
	Conc.	RSD	Conc.	RSD	Conc.	RSD		
Ca	70.47	0.40	71.31	0.90	71.55	0.70	71.11	0.80
Cl	3931	2.50	3975	2.30	3954	1.80	3953	0.56
K	78.24	1.50	78.42	0.80	78.23	1.40	78.30	0.14
Mg	23.05	0.90	22.94	1.40	23.05	1.10	23.01	0.28
Na	3194	1.10	3150	1.10	3143	0.50	3162	0.87

Results for Sample S2, no dilution:

Element	Measurement 1		Measurement 2		Measurement 3		Mean conc.	RSD (%)
	Conc.	RSD	Conc.	RSD	Conc.	RSD		
Ca	71.37	0.80	71.61	0.90	70.82	0.65	71.27	0.57
Cl	4060	2.10	3910	1.20	3926	1.20	3965	2.08
K	80.92	0.60	79.91	1.20	80.62	0.45	80.48	0.64
Mg	23.03	0.90	23.23	0.70	23.21	0.60	23.16	0.48
Na	2288	0.15	2290	1.10	2349	0.90	2309	1.50

Results for Sample S1, with dilution:

Element	Measurement 1		Measurement 2		Measurement 3		Mean conc.	RSD (%)
	Conc.	RSD	Conc.	RSD	Conc.	RSD		
Ca	70.91	0.35	71.00	0.50	71.15	0.65	71.02	0.17
K	78.90	1.20	78.30	0.45	78.80	0.85	78.67	0.41
Mg	22.81	0.90	22.26	0.30	22.32	0.80	22.46	1.34
Na	3163	0.95	3125	0.25	3184	0.45	3157	0.95

Results for Sample S2, with dilution:

Element	Measurement 1		Measurement 2		Measurement 3		Mean conc.	RSD (%)
	Conc.	RSD	Conc.	RSD	Conc.	RSD		
Ca	70.26	1.30	71.00	0.30	71.18	0.20	70.81	0.69
K	81.23	0.75	80.93	1.10	81.30	0.85	81.15	0.24
Mg	22.43	0.70	22.65	0.65	22.62	0.45	22.57	0.53
Na	2344	0.75	2391	0.60	2352	0.90	2362	1.06

Note: Chlorine was not measured in the diluted samples because the 725 nm Cl line was not sufficiently sensitive. In the diluted samples, the JY Far UV Option would be necessary to measure Cl at the 134 nm line. This is the most sensitive line for Cl and gives an LOD < 200 ppb.

3.2.3 Prospect

This report shows that the ICP-OES is a suitable technique for the direct analysis of dialysis solutions. The precision for the major elements can be further improved by using Yttrium as an internal standard. Dilution is not necessary because of the argon humidifier, sheath gas and the large internal diameter of the injector. Because of these three features, solutions with very high levels of salts can be run without problems.

4 Spark Optical Emission Spectroscopy

In 1977, the same year as the introduction of the JY 38 ICP, JY introduced several systems based on a one-meter polychromator. These included an ICP model, the JY 48P, a spark emission model, the JY 48 E and a system that had a spark stand and an ICP torch either of which could be viewed by moving a mirror, the JY 48 PE. Spark Emission spectrometry is a much older technique than ICP. It employs an electrode that contacts a solid sample and generates a high-energy spark, which creates atoms and excites them at the same time. The emission is viewed by an array of photomultipliers and the time for an analysis is very short (< 10 sec).

The technique is most commonly used in the metals industry (foundries, steel plants, etc.) where a rapid analysis is needed before the metal is cast from a furnace. The technique does not require a sample to be dissolved as is normally the case with ICP, but the sample must be homogenous and conductive. It is also not as sensitive as ICP, but it has the advantage of speed and ease of use when the sample and analytical requirements are appropriate.

In 1980, JY introduced the JY 32 Spark Spectrometer with a 0.5 m polychromator, which has evolved into today's Metalys Spark Spectrometer (Fig.4). This same polychromator was later utilized in the JY 70 ICP, which won an IR 100 award in 1981 as the first combination simultaneous-sequential ICP system.

Fig.4 Metalys Spark Spectrometer

5 Glow Discharge-Optical Emission Spectroscopy

In the mid 1980s, JY began to develop instrumentation for the new technique of Glow Discharge (GD-OES). Like ICP, this technique was the result of the development in the 1960s of a new means of creating atoms and exciting them so they could be measured optically - the Grimm lamp.

5.1 Principle of GDS-OES

GD-OES works with solids. The sample is mounted externally and mechanically sealed onto the lamp (Fig.5). A primary vacuum is established and a low-pressure gas (typically Ar) is introduced into the lamp. Then the sample is placed at an RF potential, which provides energy and creates a glow discharge. Sputtering of the sample is made by bombardment with argon ions. The sputtered atoms are then excited by collisions in the discharge and emit light signals recorded and analyzed by the spectrometer.

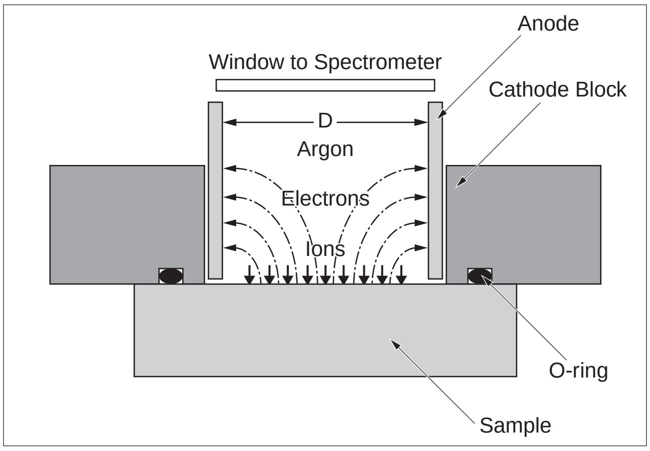


Fig.5 Grimm Lamp

Due to JY's efforts and collaboration with researchers, a unique RF source was developed. Unlike the original DC source, it is applicable to conductive and non-conductive materials. It also allows the measurement of profiles of concentration versus depth for all elements including the gasses (N, O, H, Cl) and thus allows measurement of coatings, thermal treatments, and thin and thick films. Due to this source, JY describes the technique as RF-GD-OES.

Fast and easy to operate (as it does not require high vacuum or tedious sample preparation), it is an excellent alternative to spark or X-ray fluorescence for bulk analysis. JY produces two models today. They differ in the focal length of the polychromator - 0.5 m in the GD-PROFILER™ and 1.0 m in the GD PROFILER HR. These are variations of those used in the ICP and Spark Systems. Either system can also be fitted with a monochromator for researching samples or determining elements not available on the polychromator.

RF-GD-OES is an ISO recognized technique able to perform bulk and depth profile analysis of all sort of materials. One of many industries where RF-GD-OES is making a unique contribution is the automotive industry where it has been recognized in many central automotive laboratories as a key tool for their day-to-day work.

5.2 Application of RF-GDS-OES for the Automotive Industry

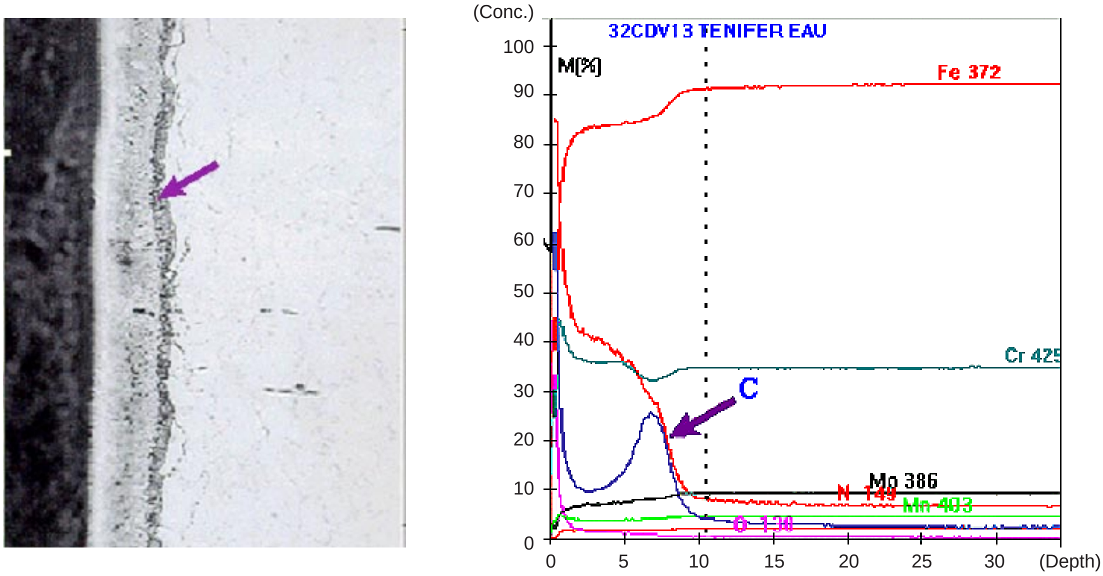
Table 6 provides examples of the breadth of analytical opportunities in just the automotive area.

Table 6 Applications in the Automotive Area

Application	Description
Base metals	Chemical composition of all metals and alloys (Fe, Al, Zn, Mg)
Steel Cleanliness	Surface carbon. Excellent correlation with the reference Ford method
Ceramic coatings	Engine antiwear coatings*
Zn coatings	All Zn coatings can be characterized (ISO norm in progress)
Organic coatings (Bonazinc, etc.)	Composition and behavior of the coatings*
Phosphatations	Control of phosphatations
DLC coatings	Hard coatings used for instances in Formula 1
Corrosion studies	Identification of defects; studies of new processes*
Cataphoresis	Control of cataphoresis bathes and coatings*
Glasses	UV protection coatings on glasses*
Benchmarking	Comparative study of all parts of competitive cars*
Presence of Cr^{+6}	Environmental issues
Painted car bodies	In depth analysis of a car body down to 200 microns*

* Indicates non-conductive or possible non-conductive layers. They account for more than 50 % of the work done in an automotive laboratory.

An example of RF-GD-OES analysis is given hereafter (courtesy of Renault SA, France) together with the SEM analysis of the same thermally treated steel (Fig.6). The various phenomena occurring near the sample surface are easily determined and quantified with the RF-GD.



(a) SEM analysis

(b) RF-GD-OES analysis

Fig.6 Analysis of the Thermally Treated Steel

6 Conclusion

When the broad range of optical emission techniques for elemental analysis of JY are combined with the EMIA, EMGA, SLFA, MESA, etc. systems of our parent company, HORIBA, we can provide a very broad range of solutions to the analyst. By working together on the development of new products such as the ULTIMA 2, the best skills of HORIBA and JY can be used to create a superior product for our customers.

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