

INDUCTIVELY-COUPLED PLASMA SPECTROSCOPY

BACKGROUND

The purpose of this article is to explain in fairly basic terms to the non-technical reader the principles behind one of the most important tools used in the routine analysis and quality control of lubricants, namely inductively-coupled plasma spark emission spectroscopy (ICP).

Most readers will be aware of the fact that the majority of liquid lubricants contain additives in addition to the lubricant base fluid. The purpose of an additive is to either improve a desirable characteristic of the base fluid, or to impart new characteristics not originally present in the base fluid.

The concentration levels of additives in the fluid are critical for a number of reasons, and their accurate measurement is one of the major concerns of the typical lubricant analytical laboratory. Firstly, additive levels in newly-manufactured lubricants must be present at pre-determined minimum levels or above to ensure that the product meets any claimed performance specification. Adequate levels to meet the requirements are established by extensive testing of a series of candidate formulations containing varying levels of additives. Secondly, although minimum levels must be at least met in newly-manufactured lubricants, the extent of over-addition must be carefully controlled since most additives are extremely costly compared with the base fluid, and over-addition will reduce profitability without incurring any consequent benefit. Thirdly, by establishing the levels of additives in used lubricants, it is possible to predict whether the useful life of the lubricant has been exceeded, and whether it is desirable to extend the useful life by selective 'topping up' of any of the additives present. It is also possible to examine used lubricants for the presence of wear elements originating from the equipment rather than the lubricant, and, by analysing trends, assess the equipment for condition and potential failure.

BRIEF DESCRIPTION

So, what is ICP and how does it work?

Briefly, when atoms of chemical elements are heated up to a certain temperature, they emit light of frequencies which are characteristic of that particular element. All elements consist of atoms, which are comprised of a nucleus surrounded by electrons, which rotate about the nucleus in fixed orbits. If sufficient energy is applied to the atom, some of the electrons move up to a higher orbit, absorbing energy in the process. When the energy source is removed, the electrons that had been elevated to higher orbits then fall back into their original orbits, emitting energy in the form of light during the process. However, the light emitted in this situation is not the normal multi-frequency 'white' light, but instead consists of a number of fixed frequencies which are characteristic of the particular element involved. Most of us will recall the strong yellow colour imparted to a Bunsen burner flame when salt (containing sodium) is sprinkled into the flame. In this case, the energy (heat) of the flame is sufficient to drive the electrons present in the sodium atoms to a higher orbit, and when they decay to their original orbit on leaving the hot flame they re-emit the energy in the form of light, the wave-lengths of which fall largely into the visible yellow range of the spectrum. This general principle was recognised many years ago, and was used in gas mantles such as the 'limelight' lamps used in theatres, also the acetylene lamps of early motor vehicles.

Although the elements sodium, potassium, lithium, etc., have comparatively low activation energies which are exceeded by the

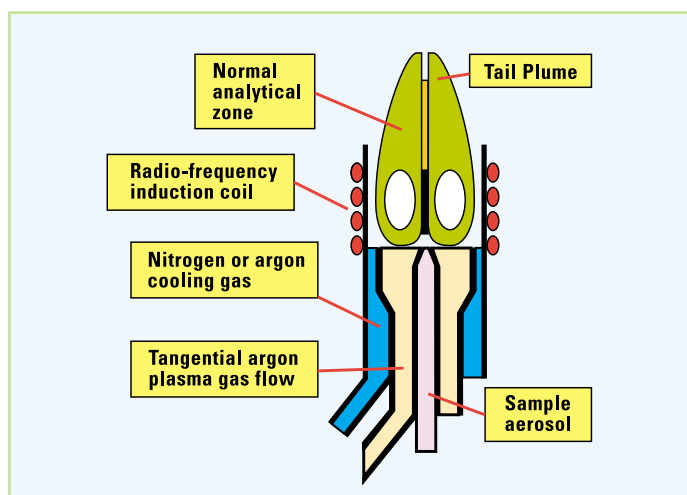
temperatures of the Bunsen flame, this is not true for the majority of other elements, which need much higher temperatures to energise the electrons to such an extent that they move to a higher orbit.

ICP hardware is designed to generate a plasma, which is a gas in which atoms are present in an ionised state, at temperatures of many thousands of degrees C. Under these intense conditions, the electrons of virtually all elements become elevated to higher orbits, and therefore emit light of characteristic frequencies when decaying back to their original states. The spectrum of the radiation emitted is split by frequencies using a conventional spectrometer, and the intensity of radiation at the various frequencies is measured using a photomultiplier.

ICP DETAILS

Typically, an ICP spectrometer emission unit consists of three concentric tubes, most often made of silica. These tubes, termed outer loop, intermediate loop, and inner loop, collectively make up the torch of the ICP. The torch is situated within a water-cooled coil of a radio frequency (r.f.) generator. As flowing gases are introduced into the torch, the r.f. field is activated and the gas in the coil region is made electrically conductive. This sequence of events forms the plasma.

The formation of the plasma is dependent upon an adequate magnetic field strength and the pattern of the gas streams follow a particular rotationally symmetrical pattern. The plasma is maintained by inductive heating of the flowing gases. The induction of a magnetic field generates a high frequency annular electric current



within the conductor. The conductor, in turn, is heated as the result of its ohmic resistance.

In order to prevent possible short-circuiting as well as meltdown, the plasma must be insulated from the rest of the instrument. Insulation is achieved by the concurrent flow of gases through the system. Three gases flow through the system; the outer gas, the intermediate gas, and the inner or carrier gas. The outer gas is typically argon or nitrogen. The outer gas has been demonstrated to serve several purposes including maintaining the plasma, stabilizing the position of the plasma, and thermally isolating

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the plasma from the outer tube. Argon is commonly used for both the intermediate gas and inner or carrier gas. The purpose of the carrier gas is to convey the sample to the plasma.

An ICP spectrometer therefore typically includes the following components:

- Sample introduction system (nebuliser)
- ICP torch
- High frequency generator
- Transfer optics and spectrometer
- Computer interface

An ICP requires that the elements, which are to be analysed to be in solution, normally water. However, since lubricants are almost entirely oil-based, it is normal to determine the additive levels directly in the lubricant without resorting to ashing followed by dissolving the ash in aqueous solution. At the additive levels typically present in most lubricants, it is normal to accurately dilute the lubricant with a suitable solvent prior to measurement because of the extreme sensitivity of the technique. Solid contaminants must be removed, as clogging of the instrumentation can occur.

The sample in liquid form is pumped at 1ml/min, usually with a peristaltic pump, into a nebuliser, where it is converted into a fine aerosol with argon gas at about 1l/min. The fine droplets of the aerosol, which represent only 1-2% of the sample, are separated from larger droplets by means of a spray chamber. The fine aerosol then emerges from the exit tube of the spray chamber and is transported into the plasma torch via a sample injector.

The light emitted by the atoms of an element in the ICP must be converted to an electrical signal that can be measured quantitatively. This is accomplished by resolving the light into its component radiation (nearly always by means of a diffraction grating) and then measuring the light intensity with a photomultiplier tube at the specific wavelength for each element line. The light emitted by the atoms or ions in the ICP is converted to electrical signals by the photomultiplier in the spectrometer. The intensity of the electron signal is compared to previous measured intensities of known concentration of the element and a concentration in the sample is computed. Each element will have many specific wavelengths in the spectrum, which could be used for analysis. Thus, the selection of the best line the analytical application in hand requires considerable experience of ICP wavelengths.

Advantages of using an ICP include its ability to identify and quantify all elements with the exception of argon; since many wavelengths of varied sensitivity are available for determination of any one element, the ICP is suitable for all concentrations from ultra-trace levels to major components; detection limits are generally low for most elements with a typical range of 1 - 100 µg /litre. Probably the largest advantage of employing an ICP when performing quantitative analysis is the fact that multi-elemental analysis can be accomplished, and quite rapidly. A complete multi-element analysis can be undertaken in a period as short as 30 seconds, consuming only 0.5 ml of sample solution. Although in theory, all elements except argon can be determined using an ICP, certain unstable elements require special facilities for handling the radioactive fume of the plasma. Also, an ICP has difficulty handling halogens; special optics for the transmission of the very short wavelengths become necessary.

Commonly-used lubricant additive elements (shown in the following table).

ELEMENT	SYMBOL	SOURCE
Barium	Ba	Detergent
Magnesium	Mg	Detergent
Calcium	Ca	Detergent
Sodium	Na	Detergent
Boron	B	Detergent
Phosphorus	P	Anti-Wear
Zinc	Zn	Anti-Wear
Molybdenum	Mo	Anti-Wear
Silicon	Si	Anti-Foam
Sulphur	S	Extreme Pressure EP
Lead	Pb	Extreme Pressure EP

Typical Contamination and Wear Elements

ELEMENT	SYMBOL	SOURCE	ELEMENT	SYMBOL	SOURCE
Silicon	Si	Dirt	Boron	B	Coolant
Sodium	Na	Coolant	Lithium	Li	Grease
Potassium	K	Coolant	Aluminium	Al	Dirt
Chromium	Cr	Ring, seals & Bearings	Aluminium	Al	Pistons & bearings
Molybdenum	Mo	Ring & seals	Aluminium	Al	Accessory drives
Copper	Cu	Bearings, bushes	Aluminium	Al	Thrust washers
Copper	Cu	Thrust washers	Copper	Cu	Clutch discs
Lead	Pb	Bearings	Copper	Cu	Turbo & cooler
Tin	Sn	Bearings	Lead	Pb	Cooler and leaded petrol
Nickel	Ni	Compressor tube	Titanium	Ti	Dirt and paint
Nickel	Ni	Steel component	Manganese	Mn	Castings
Silver	Ag	Bearings	Manganese	Mn	Steel components
Vanadium	V	Fuel oil	Vanadium	V	Valve stems
Phosphorus	P	Phosphor bronze	Vanadium	V	Steel components
Chromium	Cr	Hydraulic rods	Silicon	Si	Clutch discs

Detection Limits and Wavelengths of some typical commonly used elements

The detection limits quoted (µ/litre = parts per billion) are those applicable to the element in aqueous solution.

Care must be taken when using ICP to detect wear elements and contamination levels, since the technique is only appropriate for the measurement of elements in solution, or dispersed as very small particles (less than 3µ). Since wear debris particles normally range from <1µ to >30µ the use of ICP will only detect a small fraction of the total element present. In these situations, it is necessary to ensure that all contaminants are in true solution, e.g. using wet oxidation acid digestion, before analysis, normally using more conventional atomic absorption spectroscopy.

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ELEMENT	WAVELENGTH (nm)	DETECTION LIMIT (μ l)
Aluminium	308.215	45
Antimony	206.833	32
Barium	455.403	2
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Silicon	288.158	58
Silver	328.068	7
Sodium	588.995	29
Vanadium	292.402	8
Zinc	213.856	2

ADVANTAGES OF ICP SPECTROSCOPY

Many elements (up to 70 in theory) can be determined simultaneously in a single sample analysis.

Instrumentation is readily amenable to automation, thus enhancing accuracy, precision and throughput.

High instrumental productivity permits very competitive pricing of analytical packages, thus giving the explorer a significant return on a relatively small expenditure.

Electronic data capture and transfer to the LIMS (Laboratory Information Management System) ensures that no manual data transcription errors occur.

ICP offers a useful working range over several orders of magnitude.

LIMITATIONS OF ICP SPECTROSCOPY

Complex instrumentation requires highly skilled staff both for routine operations and for repairs and maintenance.

The emission spectra are complex and inter-element interferences are possible if the wavelength of the element of interest is very close to that of another element; for example, one of the phosphorus wavelengths suffers from both copper and aluminum interference.

As with atomic absorption spectroscopy, if solid components are present, the sample to be analysed must be digested prior to analysis in order to dissolve the element(s) of interest.

Rigid temperature and humidity control is required for best stability of the spectrometer.

Further Developments

The basic system described above is now only the starting point for a number of further developments. The efficiency of the Inductively Coupled Plasma system in producing singly-charged positive ions for most elements makes it an effective ionisation source for subsequent elemental identification and quantification using other techniques, notably mass spectrometry, where elements and particularly their

isotopes can be identified and quantified. Inductively coupled plasma-mass spectrometry is unique among the flame and plasma spectroscopy techniques in the ability to discriminate between the mass of the various isotopes of an element where more than one stable isotope occurs. (An isotope of an element is an atom with the same atomic number, but of a different mass due to the presence of additional neutrons within the nucleus compared with the parent atom). Isotope dilution, in which the change in isotope ratio for two selected isotopes of an element of interest is measured in a solution after the addition of a known quantity of a spike that contains enrichment of one of the isotopes, permits calculation of the concentration of the element. Isotope dilution is the most reliable method of accurate determination of elemental concentration. The conventional method of sample introduction for inductively coupled plasma-mass spectrometry is by aspiration, via a nebuliser, into a spray chamber. A small fraction of the resulting aerosol is swept by argon into the torch. Approximately 1 ml of sample is required per analytical run, about 99% of which is wasted.

Recently, low cost, low uptake rate, high efficiency nebulisers have been employed to combat this problem. The high efficiency nebuliser operates more efficiently at 10-200 l/min. The detection limits and precision obtained with the high efficiency nebuliser are superior to conventional nebulisers.

In practice, a two- or three- stage differentially pumped interface is used to progressively transfer ions from the atmospheric pressure plasma into the low-pressure mass spectrometer. Ions pass through a cold sampling cone (typically Ni) with an orifice approximately 1mm in diameter. The gas expands behind the first orifice, and a portion passes through a second orifice in the skimmer cone. A series of ion lenses, maintained at appropriate voltages, are used to direct the ions into the quadrupole mass analyser. The ions are transmitted through the quadrupole on the basis of their mass to charge ratios and then detected by an electron multiplier.

The use of a quadrupole mass analyser gives better than unit mass resolution over a mass range up to $m/z=300$. The inductively coupled plasma-mass spectrometry system is considered a sequential multielement analyser that has scan times less than 20 ms for one sweep. The signal intensity is a function of the number of analyte ions in the plasma and the mass-dependent transport through the mass spectrometer.

The most important advantages of ICP-MS include multi-element capability, high sensitivity, and the possibility to obtain isotopic information on the elements determined. Disadvantages inherent to the ICP-MS system include the isobaric interferences produced by polyatomic species arising from the plasma gas and the atmosphere. The isotopes of argon, oxygen, nitrogen, and hydrogen can combine with themselves or with other elements to produce isobaric interferences. ICP-MS is not useful in the detection of nonmetals.

However, this technique is of limited value to the lubricants formulator, being more appropriate to research uses, particularly in the field of environmental science.

Summary

The adoption of conventional ICP has revolutionised the ability of the lubricant manufacturer to blend products with a degree of control such that specifications are reliably met; yet quality giveaway is reduced to the absolute minimum. However, in spite of its widespread adoption within the lubricants industry, the principles of the technique are not generally well understood by most, apart from those intimately associated with its operation.

David Margaroni

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EMBRACING INFORMATION TECHNOLOGY AND THE INTERNET REVOLUTION FOR LABORATORY SERVICES

There are many factors that can affect the performance of a business. Some are straightforward and relatively easy to deal with, like a piece of equipment requiring repair or the introduction of a new process, while others are complex such as the impact of war or the introduction of a new currency.

Businesses are more likely to succeed if they are able to detect the emergence of these factors in order that they can quickly deploy their resources to handle the changing environment.

This is especially true for the suppliers of laboratory services to the oil and petroleum sectors. Traditionally the keys to success for oil and petroleum laboratories per se have centred on what could be done "at the bench." Consequently, market leaders have focused on quality accreditations (ISO and UKAS), the qualifications and experience of their laboratory staff as well as impressive lists of sophisticated laboratory equipment.

These attributes are still, of course, very important when deciding who will perform your oil testing. But, increasingly customers require a more creative and innovative service that adds value to their business. Vernolab believe that these requirements are attainable with the use of Information Technology (IT) and the Internet.

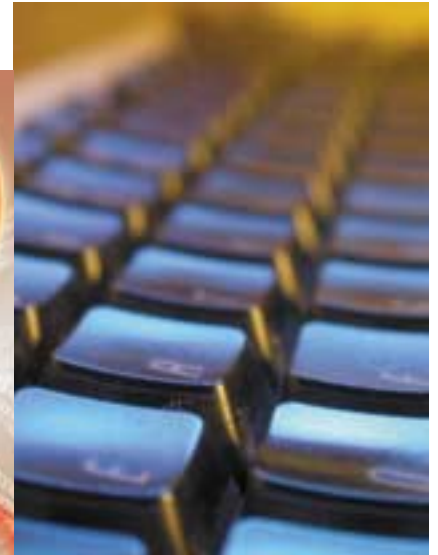
Here are a just a few examples of how a laboratory service provider and the customer can use the power, diversity and sophistication of IT and the Internet.

Web Technology allows: -

- enquiries of a technical or commercial nature to be quickly re-directed to the appropriate person allowing a fast response to the customer
- registration of information related to the samples by the customer prior to arrival at the laboratory
- tracking of progress of laboratory analysis
- interrogation of historical data to identify trends
- easy viewing, printing and distribution of final reports
- confidentiality and selective access to data through password protection system
- protection of data in the event of catastrophic failure, i.e. fire
- re-branding of service provider web page to allow customer to sell service and hide the identity of the service provider
- the service to be sold across country borders
- the service provider to trade with suppliers, including chemical suppliers, banks, travel companies etc. on-line to minimize administration costs.

Software

QA software to manage ISO 9001:2000 requirements allowing easy access to the QA system by all users thus ensuring consistency, improving quality and minimizing administration costs.



Intelligent software (for used oil services) to allow interpretation of scientific data to enable early identification of trends allowing prediction of equipment and /or oil failures and maximizing customer productivity.

Hardware

Laboratory equipment linked to the business computer network allowing transfer of scientific data, minimizing reporting delays and reducing potential transposition errors.

Computer terminals throughout the business allowing fast and effective flow of information.

You may have seen a commercial for one of the leading banks explaining that through the use of the Internet we can all be bank managers. Perhaps through the use of the internet we now can all be laboratory managers. Pass me the test tube please!

Vernolab are part of the PCAS (Produits Chimiques Auxiliaires et de Synthèse) Group and provide petroleum and lubricant testing services to a range of market sectors. Vernolab currently have 3 sites, two in France and one in Stanlow, near Ellesmere Port. Our facility at Stanlow provides a comprehensive used oil testing service including provision and design of sample kits through to laboratory analysis in addition to sophisticated reporting systems. Vernolab UK also provide QC testing in support of production for BP Castrol's Stanlow site.

LINK

Paul Parkinson Tel: +44 (0)151 348 6802
Email paul.parkinson@vernolab.co.uk