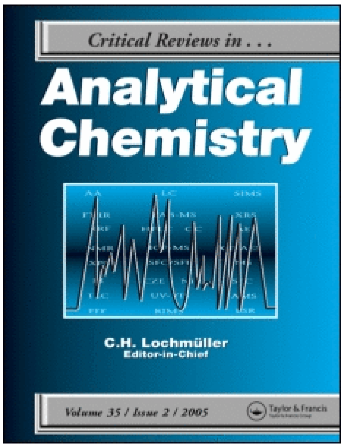

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Wear Metal Analysis of Oils

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Wear Metal Analysis of Oils

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This article concentrates on reviewing the literature related with wear metal analysis of oils. An overview on the existence of metals in oils and typical wearing situations is discussed briefly. Different pre-treatment methods of oil samples before wear metal analysis are presented with application remarks. Common measurement techniques of wear metal analysis, both qualitative and quantitative, are handled and compared with each other.

Keywords wear metals, oils, measurement techniques, pre-treatment methods

INTRODUCTION

It can be said that modern industry rests on a layer of lubricant. If it is not able to separate moving machine elements from each other, wearing will be inevitable. Wearing causes significant expenses to industry. There are evaluations that expenses due to friction and wear amount up to several billion euros annually in different countries (1). Evaluations have been carried out in USA, England and Germany, and the estimate was that expenses range between two to seven percent of the gross national product (GNP) (1). These expenses are calculated to be as high as 2.7 billion euros a year in Finland only, nearly one third of which could be saved by applying the latest tribological knowledge (2). Detaching particles from machine elements circulate in the lubrication system unless captured by oil filters, or unless they sink to the bottom of oil tanks. Lubricating oil can tell not only about its own condition, but also about the condition of the studied machine. Just as a blood test can reveal illnesses in people, a lubricating oil analysis can reveal “illnesses” in machines. There are numerous different oil analysis methods available, but those that indicate the wearing of machine elements are mainly metal analyzes and solid debris analyzes of oils. A metal analysis indicates both the increasing amount of wear metals and the decreasing amount of additive metals, thus indicating machine defects or an insufficient lubrication efficiency of oil. Metal analysis is an important tool in predicting maintenance. This review concentrates mainly on wear metal analysis and its applications in machine diagnostics. It is not meant to be an all-embracing report discussing all the relevant literature involving wear metal analysis of the past 60–70 years, but rather achieves to gather different wear metal analysis techniques and methods into one report. Comments on typical metals present in oils are presented in the following Section. Oils are often complex and viscous in nature, therefore pre-treatment methods of oil samples are often required before a metal analysis; these methods are discussed in the third Section. The measurement techniques available for qualitative and quantitative metal analysis are presented in the fourth Section.

THE EXISTENCE AND SOURCES OF METALS IN OILS

Wearing may be oil-, machine- or installation & maintenance related. Oil-related problems may be caused by lubricant starvation, degradation or contamination. Machine-related problems can result from too high speeds, overloading or high temperatures. On the other hand, machine elements may be misaligned or unbalanced, and thus finally cause wearing. One should keep in mind that these problems can be observed singly or as combined, as well as simultaneously or sequentially. Machine wear

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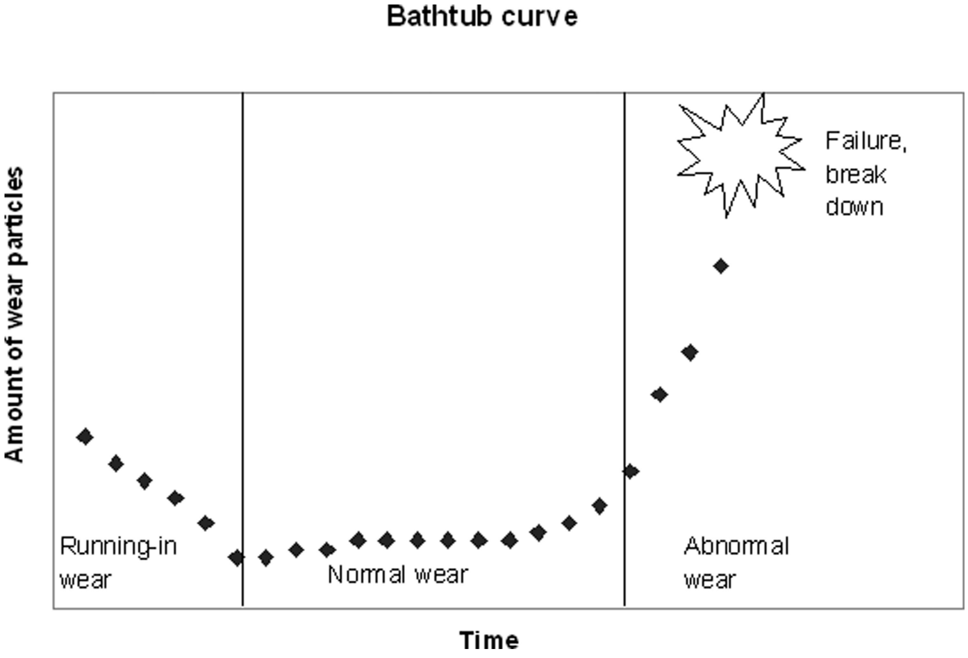

FIG. 1. A bathtub curve.

is often represented with a so-called bathtub curve, in which the machine first experiences running-in-wear, then slight normal wear, and finally fast abnormal wear, eventually leading to a catastrophic failure. Naturally, other types of wearing phenomena are possible for different types of machines. Figure 1 represents an idealized situation for typical machines (3,4).

The wear mechanisms that detach particles from metal surfaces are numerous. Varying conditions favor varying wear mechanisms, although there is considerable overlapping as well. Wearing can be divided into two main types based on the relative motion that is causing the wearing phenomenon, or based on the physical or chemical wearing mechanisms. Motion types that cause wearing are sliding, rolling, impact loading, vibration, and liquid flow with or without solid particles. The wearing mechanisms used to differentiate types of wearing are adhesion, abrasion, surface fatigue, and tribochemical wearing (4). Studying wear rates and wearing mechanisms not only reveals the wearing machine element, but may also give an estimate of its remaining lifetime. If wearing is detected at an early stage, machine repair can be planned well in advance, thus avoiding unnecessary maintenance expenses and related production delays. The occurrence of different wear metals in lubricating oils naturally depends on the machine studied and the materials of its components. Table 1 gathers sources for certain elements in oils; it has been modified from information given as references (3–5).

Different types of wearing mechanisms introduce particles with different physical and chemical properties into oil. Metals can exist in oils in three different forms: as metallic particles, as organo-metallic compounds or as metal oxides. Metallic particles and metal oxides may be produced in wearing situations. Organometals may be produced in reactions between oils and metallic surfaces or wear debris. Fast reactions between wear debris and oils are often due to the aptitude of wear debris to catalyze degradation reactions of oils. On the other hand, additive metals appear usually as organometals in oils, e.g. as “metal soaps” (6). The types of wearing also affect the chemical nature of wear debris. Adhesion, for instance, produces completely different types of particles than corrosion does. This is discussed in detail by Roylance and Hunt (4). Besides its source, the chemical form of wear debris also affects its particle size distribution. Organometals and metal oxides are often in the sub-micron size class, whereas metallic particles can be several or even hundreds of microns in size. The occurrence of different chemical forms and particle size distributions of metals depend on the metal and oil studied. Kauffmann et al. (6) studied copper, iron and magnesium in used ester-based lubricating oils. They observed that

TABLE 1
Certain sources for various elements in oils

Source	Elements
Bearings	Al, Ag, Ca, Cr, Cu, Fe, Ni, Pb, Sb, Sn, Ti, Zn
Gears	Ag, Cu, Fe, Mg, Ni, Sn
Shafts	Ag, Fe, Cr, Mg
Seals	B, Cr, Pb, Si, Sn, Zn
Contaminants	Al, B, Ba, Ca, Cr, Cu, K, Mg, Na, P, Si, V, Zn
Greases	Al, Ba, Ca, Li, Na, Ni, Pb, Si, Sb, Zn
Oil additives	Ba, B, Ca, Mg, Mo, Na, P, S, Si, Sn, Zn

copper is usually present as submicron particles except in oil samples obtained from machine failure situations. Magnesium existed almost entirely (95%) as metallo-organic species in the studied samples. The chemical form of iron depended on the condition of the machine, thus in samples of machine failure iron was usually found in organometallic or metallic form, and in normal wear cases as ferric oxide. The chemical nature and size of wear debris affect the chosen measurement technique. For instance, direct dissolution of oils with organic solvents and flame atomic absorption spectrometer (FAAS) or inductively coupled plasma-optical emission spectrometer (ICP-OES) determination can not be used if samples contain large amounts of bigger particles (>10 μm, the absolute value depends on the literature cited and the technique used) (6–12).

PRE-TREATMENT METHODS OF OIL SAMPLES BEFORE WEAR METAL ANALYSIS

Most of the measurement techniques require that the sample is in the form of a solution. The sample must not contain high amounts of insoluble particles and its viscosity must not be too high. These requirements affect the choice of the pre-treatment method, most of which are relatively labor intensive, especially when numerous samples are analyzed. There is therefore a continuous development of more simple and versatile methods.

None or Minimum Pre-treatment

Certain measurement techniques do not necessarily require a complicated pre-treatment of oil samples. These include, for example, porous cup and rotating electrode emission spectrometers, X-ray fluorescence (XRF) spectrometers, neutron activation analysis, ferrography, laser induced-breakdown spectroscopy (LIBS), or laser ablation (LA) attached either to an ICP-OES, or to an inductively coupled plasma-mass spectrometer (ICP-MS). However, these methods may contain problems in calibration, because all metals can either not be measured correctly or it is very difficult to measure them. Type of oil may also complicate the measurement. These techniques are presented in more detail in the fourth Section. LA is only discussed in this section because it is not a measurement technique, but a sophisticated sample introduction method.

Laser techniques for analysis of elements in solids and liquids have been developed from the beginning of the 1960s. The first promising techniques resembled the LIBS technique because they used lasers to produce a plasma discharge on the sample surface, and the produced plasma excited and atomized/ionized the sample. The emitted radiation was determined by emission spectrometers. Although these techniques can be very reliable for some samples, they may have problems in sensitivity and precision issues, and they may suffer from matrix effects in some cases. Later on, LA started to be used only in sampling for ICP-OES and ICP-MS. Atomization, ionization and excitation could be carried out under a better control in ICP plasma. LA can be used to ablate different types of materials independent of their physical or chemical nature. Different types of lasers (wavelengths in the range of visible, IR or UV light) have been applied in LA instruments and they all have their own benefits. Results obtained by LA are affected by the wavelength of the laser used, the energy of the laser, the amount of laser pulses per second, adjustment of the laser, the diameter of the laser beam, optical absorption ability of the sample, as well as adjustments of the spectrometer. The LA method can be calibrated using similar standards as samples (external calibration), combining external calibration with an inner standard, or using solution calibration. Combination of external and internal calibration is the method usually recommended. Calibration with solutions should be avoided, because solutions do not usually resemble the samples studied. LA does not set any requirements for samples, its sensitivity and accuracy are usually good, and the sample pretreatment process as well as contamination risks are minimal. Furthermore, various polyatomic spectral interferences can be avoided, when compared with solution nebulization, when LA is coupled with ICP-MS. Precision and detection limits of the LA method attached to ICP-MS depend on the area ablated, the analysis time, the amount of analytes, transfer efficiency from the LA cuvette to the plasma, sensitivity of the detector, and the background and types of the analytes (13, 14).

Dissolution with Organic Solvents

Organic solvents have been used to dissolve oil samples for decades. This pre-treatment method is simple, easy to automate, fast to proceed with and the nature of the oil-solvent background is relatively simple requiring only minor background corrections. Calibration has to be carried out using organometal-oil standards, but they are commercially available. The use of organic solvents is especially suitable for quick check-ups of certain indicator metals. The main disadvantage of this method is that large solid particles (>10 μm) do not dissolve in organic solvents, and it causes loss of sensitivity in the nebulization, atomization and detection of wear metals by absorption and emission spectrometers. The proposed size limit depends on the instrument used as well as its properties, being nevertheless even smaller than 10 μm for flame atomic absorption spectrometer (FAAS). The influence of the particle sizes on wear metal analysis has been discussed in various articles over the years (6–12). In addition, oil solutions may form carbon deposits onto the tip of the ICP torch in ICP techniques. This can be minimised by using auxiliary argon targeted to the problematic area and optimizing the position of the torch.

In 1965, Burrows et al. (15) compared different organic solvents in the analysis of lubricating oils by FAAS. Heptane, kerosene and methylisobutylketone (MIBK) were included in the study. MIBK was observed to be the most sensitive of the studied solvents. Kerosene behaved almost as well as MIBK, but heptane disturbed the air-acetylene flame used significantly. Typical solvents in FAAS analyzes have been xylene, MIBK or their mixtures; xylene seems to be a more stable solvent in these analyzes (16–20). King et al. (16) compared results of wear metal determination by FAAS and ICP-OES with xylene dissolution. They observed that these techniques produced similar results with the pre-treatment used. Lukasiewicz and Buell (17) tested naphtolite in the zinc analysis by FAAS and observed that napholite has better burn properties and less background disturbances than normally found in other solvents. Xylene and kerosene have been used as a typical solvent with ICP-OES (16, 21), but kerosene has also been proven to work sufficiently well in the FAAS analysis, when it was compared with ICP-OES (22). Duyck et al. (23) used toluene as a solvent in the analysis of crude oils by ICP-MS and ICP-OES. Toluene has, however, poor stability in the determination of certain metals. Chromium, iron, magnesium and lead were also analyzed by FAAS using a mixture of propan-2-ol and terpentine as a dissolution solvent in the study of Barbooti et al. (24). Pignalosa and Knochen (25) used flow injection analysis (FIA) to introduce oil samples to FAAS. They first injected the oil sample into a kerosene stream. Thus both the dilution of samples and sample introduction were carried out automatically. Results of copper and iron determinations of real oil samples were compared with the analysis in which dilution was manual. The throughput of wear metal analysis with the developed method was good, and could even still be improved by software modifications. Reis et al. (26) used the FIA technique in the analysis of copper, iron, chromium and lead in lubricating oils. Chirinos et al. (27) optimized the ICP-OES instrument for oil-xylene solutions. They observed that the influence of organic solvent on ICP-OES performance was strongly dependent on the type of the emission line used and nebulizer pressure was the variable having the largest influence on the ICP operation. Berndt et al. (19) improved sample introduction in FAAS by using a high pressure hydraulic nebulizer. They used a mixture of methanol, MIBK and white spirits as a carrier solvent without any influence on the sensitivity. They also tested on-line dilutions of oil samples, because undiluted oils had problems in the nebulization. The use of high pressure nebulization eliminated the influence of sample viscosity on sensitivity, therefore lower detection limits could be achieved. Results of copper and lead concentrations in used oils were comparable with X-ray fluorescence (XRF), but results of iron were not totally comparable. Mora et al. (20) produced quite a similar study, in which they varied the oil content in oil-solvent solution as well as the nature of the carrier. They compared the obtained results using a single-bore high pressure nebulizer attached to FAAS with the use of a traditional pneumatic concentric nebulizer. They observed that isobutyl methyl ketone (IBMK) was a better carrier than methanol, and that if lubricating oils were nebulized as such lower detection limits could be achieved. The use of a single-bore high pressure nebulizer also improved the analysis throughput and reduced sample contamination risk, because sample dilution and acid digestion stages were not required. Online dilution has also been used with ICP-OES. Jansen et al. (7) used two Gilson peristaltic pumps and a double-needle system when diluting oil samples with kerosene prior to ICP-OES analysis. Kahen et al. (28) used a direct injection high efficiency nebulizer (DIHEN) with ICP-MS in the analysis of xylene-diluted petroleum samples. Dreyfus et al. (29) determined trace and ultra-trace elements in crude oil and its fractions. Fractionation was carried out by a perfluoro alkoxy (PFA) filter, which separated malthenes and asphaltenes. They used a xylene dilution for pre-treating oil samples and ICP-MS for measurements. Matrix effects were eliminated by a standard addition method in the calibration and detection limits of pg/g could be achieved. Karadjova et al. (30) compared the use of diethyl ether, IBMK, xylene, heptane and 1,4-dioxane for dissolving and diluting olive oil samples and N,N-hexamethylenedithiocarbamic acid–hexamethylammonium salt as a modifier before ETAAS analysis. IBMK and 1,4-dioxane were the most useful solvents for analyzing Al, Cd, Cr, Cu, Fe, Mn, Ni and Pb in olive oils when using ETAAS. Fernández-Pérez et al. (31) studied the use of diisobutylketone (DIBK), MIBK and kerosene as dissolution solvents before the analysis of Cu, V, Fe, Pb, Ni and Cr in used industrial oils using ETAAS. They observed that all used solvents are applicable prior to ETAAS analysis, but the best analytical performance was achieved when the oil samples were diluted using DIBK. Stigter et al. (32) applied carbontetrachloride and xylene as dilution solvents in the ETAAS analysis of Cd, Cr, Cu and Zn in crude oils.

Dry Digestion/Ashing

Ashing is carried out at a high temperature (600–800°C) in a muffle furnace. Organic material is burned and what remains is inorganic ash. The ash is dissolved with a suitable acid, or a mixture of different acids, and analyzed by a chosen technique. Burrows et al. (15) used 10–20 g of oil in the ashing stage, but the amount of oil sample required is a lot smaller (2–5 g) in the more recent studies. Goncalves et al. (33) used a method in which the treatment of an oil sample of 5 g took over five hours. The sample was first burned until it dried, after which two digestion temperatures (250°C/1 hour and 600°C/4 hour) were applied. The final residue was dissolved with concentrated hydrochloric acid. Barbooti et al. (24) used a modified dry digestion in which silica gel was used as an auxiliary substance in the digestion. Porous silica gel prevents crackling and evaporation of the sample, which helps in achieving a shorter ashing time, and an improved accuracy. Ekanem et al. (34) used sulphanilic acid as an auxiliary reagent in the ashing stage. Sulphanilic acid strengthens the release of metals in the digestion stage and increases the recovery of metals. In the ashing procedure of Udoh (35), 10 g of oil was used. The oil was ignited using a flame and allowed to burn until a coke residue was formed. Volatile substances were removed in this stage, and the residue was heated in a muffle furnace at a temperature of 900 ± 50°C until all carbon was removed. The heating lasted for ~ 3 hours. The cooled residue was treated with 20 ml of 6 M hydrochloric acid. The solution thus formed was finally concentrated to 5 ml and diluted with water. Concentrations of calcium, magnesium and zinc were analyzed using FAAS. Udoh et al. (36) presented an alternative ashing method for crude oils. They used p-xylenesulphonic acid as an auxiliary reagent. The proposed procedure uses 20 g of crude oil and 1 g of *p*-xylenesulphonic acid. The mixture is heated until it boils, then ignited and charred, after which carbon is burnt off in a muffle furnace at a temperature of 500°C. This method was tested against traditional sulphuric acid ashing and the procedure recommended by the Institute of Petroleum. The proposed method produced statistically similar results as the other two methods. It has certain benefits: *p*-xylenesulphonic acid is suitable for complex matrices, it is not highly hygroscopic as is the alternative reagent benzenesulphonic acid, the ashing time can be reduced to 5 hours, a filtration stage is not required, and the same procedure can be used in the determination of all elements without modifications. The most difficult problem in dry ashing is the evaporation of volatile metals during the sample treatment, and it is superseded by quicker and more accurate pre-treatment methods.

Wet Digestion

In traditional wet digestion, organic material is degraded using strong acids, high temperatures, and normal air pressure. The amount of oil used is a couple of grams and the samples are boiled in a digestion vessel with the chosen acids. Hydrogen peroxide may be added at the end of the digestion in order to improve digestion efficiency. The used acid or acids are evaporated, and the residue is subsequently dissolved and diluted with a mild acid. Wet digestion is quicker to operate than dry digestion (taking usually 1–3 hours). Sulphuric acid, nitric acid or hydrochloric acid alone, as sequential additions, or as mixtures are used in the different stages of digestion in the most studies. (33, 37–41) Goncalves et al. (33) proposed a modified wet digestion method, in which silica gel and calcium chloride were used as auxiliary reagents. Cook et al. (38) presented two wet digestion methods both for oils and for oil-contaminated soils. One uses nitric acid and hydrogen peroxide, the other perchloric acid instead of hydrogen peroxide. The digestion took about 10 hours in their methods. Kowalewska et al. (39) studied different pre-treatment methods of crude oil distillates done before a FAAS, ETAAS or ICP-MS copper analysis. They observed that the best pre-treatment for crude oil and heavy petroleum products was mineralization in open vessels using sulphuric acid and *n*-butanol. Mineralization in oxygen-hydrogen flame appeared to work well with gasoline samples.

Microwave-assisted wet digestion is carried out in closed, pressurized vessels using various acids or acid mixtures. Microwave digestion takes significantly less time than traditional digestion methods. In addition, better recoveries of volatile metals can be achieved, contamination is minimized, and the required amounts of reagents are relatively small. Microwaves heat up samples fast because dissolution acids effectively absorb microwave energy. Closed vessels make increased boiling points of the acids possible, due to increasing pressures. Thus, higher digestion temperatures are possible, improving oxidation and dissolution efficiencies of the acids. As a whole, the digestion procedure is very fast and efficient, lasting only significantly less than one hour instead of several hours in traditional wet digestion methods. Different variations of acids have been proposed in previous literature, but acid mixtures usually contain nitric and hydrochloric acids as recommended in the US EPA 3051 A standard (42). Nitric acid has been used e.g. by Aucélio and Curtius (43), Mora et al. (20) and Jankowski et al. (44). Jankowski et al. (44) also used sodium nitrate to prevent evaporation of phosphorus. Costa et al. (45) used nitric and sulphuric acids in the digestion and hydrogen peroxide as an auxiliary substance in their digestion method, which lasts 25 minutes. Munoz et al. (46) proposed quite a similar method. Nitric acid and hydrogen peroxide have also been used by Wang et al. (47), Souza et al. (48) and Vähäoja et al. (49). The most significant limiting factor in the microwave-assisted acid digestion is the amount of digested oil, which has to be small enough in order to prevent excessive increment of pressure in the digestion vessel. For example, Vähäoja et al. (49) used a two-stage digestion, in which pressure was released from the vessels between digestion stages. In this way, 0.5 g of oil could be used in the digestion. Digestion stages lasted 20 minutes combined, followed by the cooling stages. Wondimu et al. (50) presented a microwave digestion method for residual fuel oil. They used nitric acid and hydrogen peroxide in the digestion, but the amount of oil digested was only 0.25 g. However, on the analysis of trace elements in the NIST SRM 1634 b standards, their results were in agreement with the certified values, except on calcium and barium. Sanz-Segundo et al. (51) proposed a microwave-assisted digestion involving nitric acid and hydrogen peroxide as digestion reagents. They could use 1.0 g of oil in the digestion, but the digestion they used was rather long-lasting, involving 4 digestion stages (110 minutes) plus additional cooling stages. 1,4-dioxane had to be used for diluting digested samples to a given volume in order to avoid the existence of organic residues in the solution. Bellido-Milla et al. (52) proposed a faster pre-treatment procedure, which dissolves only the metallic particles in closed reactors applying microwaves as assistance. The proposed method involved the use of nitric acid, IBMK, isopropyl alcohol and Triton X-100 surfactant as reagents. They also compared the developed method with other methods: simple dilution, slight acid attack/dilution, and ashing. The study of Kowalewska et al. (39) indicated that microwave-assisted acid digestion may work poorly in the digestion of crude oil distillates. Hydrogen fluoride (HF) can also be used as a digestion acid, but it has been shown that HF did not have any significant influence on the digestion efficiency in the decomposition of coal samples (53, 54). It was noticed that HF could even diminish recoveries of certain metals, like Al, Ca, Mg, due to formation of insoluble fluoride precipitates.

Oil Emulsions

Emulsification of oil samples means that organic, water-insoluble samples are converted to micro-emulsions by adding surfactant to the oil sample. Another option is to prepare a homogenous micro-emulsion, i.e. a so-called three-component solution including aqueous and organic phases without a surfactant. After the oil has distributed uniformly in the aqueous phase and the sample behaves like a water solution, inorganic water-soluble standards can be used in the calibration.

Saba and Eisentraut (55, 56) proposed a "particle size independent method" for pre-treating lubricating oil samples in the late 1970s and continued this work in the 1980s (57, 58). They used organic solvents and acid mixtures; their acid mixtures always contained HF together with other acids, while their organic solvents were MIBK or a MIBK/isopropyl alcohol mixture. Emulsification was improved using warming and ultrasonification. Goncalves et al. (33) tested different emulsification methods with and without acids. It is recommendable to carry out acid treatment in order to dissolve solid metal particles. However, if metals soluble in oil are determined, then acid addition is not necessary as displayed in the study of Murillo et al. (59). Maurillo et al. (60) compared different surfactants in emulsification of sunflower oils, and observed that Tween 80 was the best of the studied surfactants. A highly sophisticated way to produce oil emulsions is the so called on-line emulsification, in which flow injection is applied. Burguera et al. (61) used on-line emulsification with ETAAS in their analysis of chromium in lubricating oils. The sample solution was injected into a hexane stream, which was then immediately mixed with sodium chloride, sodium dodecylsulphate, and butanol. An aliquot of the emulsified sample was mixed with air before sampling into the atomizer. The same research group (62) later used the same method in determining aluminium in lubricating oils. de Souza et al. (63) proposed a detergentless emulsion formation for edible oils and fats in the analysis of Cd, Co, Cr, Cu, Ni and Mn by ICP-OES. They used a mixture which had 6% oil, 64% propan-1-ol, and 30% water. Fats were dissolved first with 0.5 ml of xylene, and the mixture that was used consisted of 5% fat, 70% propan-1-ol, and 25% water. Inorganic standards could be used for calibration especially if samples were treated with nitric acid. de Souza et al. (64) also tested similar emulsification for crude oils: results were good in this case as well. They have also compared detergentless emulsification against detergent emulsions (Triton X-100 as a surfactant) in the analysis of refractory elements in diesel and fuel oils by ICP-OES (65). The observations were that both procedures were very simple and applicable with ICP-OES. Both methods also produced good results when certified materials were studied. Souza et al. (48) have also compared the use of detergent emulsions with microwave-assisted acid digestion and kerosene dilution in the analysis of refractory elements in lubricating oils by ICP-OES. They observed certain advantages using emulsification over the traditional pre-treatment methods. Wang et al. (47) proposed a fast method in which an oil/toluene mixture was mixed with concentrated nitric acid using ultrasound and heating. They also compared the proposed method with microwave-assisted acid digestion and direct dilution with isopropanol/toluene mixture. The proposed method produced results comparable with the other methods. Emulsion sample introduction of organic liquids into FAAS has been studied thoroughly by Lakatos et al. (66).

Other Methods

Vanadium, copper, nickel and iron concentrations in crude oils have been determined using high performance liquid chromatography (HPLC). However, the determined metals must be in the form of metal complexes. Khuhawar et al. (67, 68) used bis(acetylpivalylmethane)-ethylene-di-imine (H_2APM_2en) and bis(salicylicaldehyde)tetramethyl-ethylene-di-imine (H_2SA_2Ten) as complexing reagents. Crude oil samples were treated with sulphuric acid, nitric acid and perchloric acid before complexation. Complexing reagents react selectively with certain oxidation states of the metals studied, hence the metals were reduced to desired oxidation states using sulphur dioxide. The pH of the solution was adjusted to 6 using acetate-acetic acid buffer before adding the complexing agent. After that the solution was warmed, extracted with chloroform, and the organic layer was analyzed using HPLC.

Acid extraction has been used to remove metals from organic oil samples into aqueous phase in order to simplify measurements with atomic spectrometers (inorganic calibration standards, no viscosity problems, no organic carbon present). Nitric, hydrochloric and sulphuric acids as well as mixtures of hydrochloric acid and hydrogen peroxide or nitric acid have been used as extracting acids (46, 69, 70). Thiem and Watson (71) studied extraction efficiencies of emulsions for 21 elements found in oils and observed that efficiencies close to 100% can be achieved for many elements. The extraction can be improved using ultrasonification. Kowalewska et al. (39) used hydrochloric acid extraction in the copper analysis of crude oil distillates and it seemed to be an effective pre-concentration method enabling lower detection limits. However, extraction could not be used with asphaltene-containing samples.

MEASUREMENT TECHNIQUES

There are various measurement techniques available for wear metal analysis depending on the metals measured, the studied oils, performance requirements of the method, and the amount of samples studied. Typical techniques are atomic spectroscopy in its different forms (absorption and emission spectroscopy), mass spectroscopy, XRF, ferrography, microscopic techniques, chromatographic techniques, and neutron activation analysis.

Porous Cup Electrode and Rotating Disk Electrode (RDE) Spectrometers

The porous cup electrode technique was applied in lubricating oil analysis by the end of the 1940s. Gassmann and O'Neill (72) and Gambrill et al. (73) used the porous cup electrode technique for the analysis of phosphorus, barium, calcium, and zinc in lubricating oils. However, the technique was not suitable for analyzing oil samples containing solid debris. Gambrill et al. (73) also applied a rotating disk electrode for determining both the previously mentioned elements, as well as lead and iron.

Fabrication and the functioning principle of the porous cup electrode is given in detail in Feldman's article (74) from 1949. The porous electrode cup is filled with the sample including two electrodes made of special graphite rods. The cavity of the upper electrode, in which the sample is placed, is made by drilling a hole of a diameter of 3–4 mm onto the top of the graphite rod. The sample solution will then slowly drip to the bottom of the electrode. The lower electrode is placed underneath the porous cup: the spark hole is about 3 mm wide. The power supply used should have low voltage and intermittent behavior, although a synchronized spark can also be used. The spark causes degradation and magnetization of the solution. The formed emission spectrum is stored on a spectrum analysis film. The lower the concentrations of the studied elements are, the higher the variations observed. Relative standard deviations (RSD) of as good as 10% may be achieved nevertheless.

The rotating disk electrode contains a so-called "feed electrode" attached to a vertical shaft. The feed electrode made of crystalline graphite is embedded in the studied solution. The vertical shaft constantly rotates and the sample solution moves to the upper part of the disk. An opposite graphite electrode is placed above the disk, and it rotates to the opposite direction to the feed electrode. The high temperature arc required in the rotating disk electrode systems can be produced by using either a high voltage alternating current formed by a group of capacitors, or a low voltage alternating current source ignited by high voltage pulses. Direct current can also be applied. Detection of the elements is carried out by an emission spectrometer. Results comparable with the porous cup electrode can be achieved, the measurement range being on the mg/kg range and RSD values being 10%. The performance of a certain RDE-OES instrument depends on the arc, the background correction, the burn time, the viscosity of the samples, as well as the particle sizes of the studied metals (3). On the other hand, RDE-OES is a low-cost technique requiring only replacing of the rod and the disk electrodes, it has good precision and repeatability, measurements are fast, and samples do not require pre-treatment. Problems related with RDE-OES techniques are matrix interferences and the possible quick settling of metal particles in oils (3, 9, 75).

However, Guinat (9) proposes that matrix interferences can be eliminated with a careful planning of the analysis. Separate calibration curves have to be produced for mineral and synthetic oils. The rapid settling of metal particles is a problem with metal powders suspended in lubricating oils. Guinat's (9) observation was that wear metal particles produced in natural ways do not tend to settle in short periods of time. The only significant problem is that particles $>8\ \mu$m can not be recovered sufficiently well in the analysis. Kauffmann (10) proposed a method based on the RDE-OES technique that can be used in performing qualitative particle size distribution and particle composition analyzes. The method can distinguish between dissolved wear species produced by normal wear (up to 1 μm) and abnormal wear particles (over 3 μm). For instance, the indication of a failure was mainly detected as the presence of 8 μm particles in used oils and not as high concentrations of wear debris in this study. Naturally, the accuracy of the particle size distribution analysis is dependent on the capability of the RDE-OES.

Atomic Absorption Spectrometers (AAS)

In AAS techniques (76) the sample solution is nebulized or injected into an excitation source that atomizes the elements of the sample. Atoms of the studied sample are radiated by a hollow cathode lamp which emits ultraviolet (UV) or visible light at the characteristic wavelength of the studied element. The amount of light absorbed depends on the amount of atoms of the studied element in the sample. The degree of absorption is detected and converted to concentrations when compared with a calibration series. AAS techniques are often grouped based on the atomization method. The most common way to atomize a sample is flame (FAAS). The flame can be produced using different gas mixtures of which air-acetylene and N_2O-acetylene mixtures are the most common. Composition of the flame affects its temperature and quality (oxidizing or reducing conditions), and the flame to be used is selected based on the atomization requirements of the studied elements. In the graphite furnace AAS (GFAAS), nowadays called the electrothermal AAS (ETAAS) technique, the sample is atomized in a small graphite tube using electric current for heating. Most of the wear and additive elements of lubricating oils can be analyzed using FAAS or ETAAS. Special techniques are available for certain elements, e.g. cold vapor AAS (CVAAS) for mercury and hydride techniques for selenium, arsenic, antimony, bismuth, germanium, tin and lead. The main drawback of AAS techniques is their sequential nature; the hollow cathode lamp is specific for a certain element and has to be changed between measurements of different elements. AAS techniques are most suitable when only a few elements are measured and the amount of samples is not very big, e.g. in the case of detecting certain indicator metals of wearing (22). Certain elements, so-called refractory elements, form stable oxides and are difficult to analyze using FAAS. Spectral interferences are typically minor with FAAS. All in all, FAAS is a suitable and widely applied method for wear metal analysis of oils (6, 8, 15–20, 22, 24–26, 33–36, 38, 51, 52, 55–58, 66). de la Guardia and Salvador (18) presented a good review of using FAAS in lubricating oil analysis in 1984. They gathered 104 references and presented the typical pre-treatment methods of oil samples with application remarks. They also discussed the amount of published articles on FAAS from 1940 to 1981 and the popularity of this subject. ETAAS techniques have become more popular in the 1990s, and their benefits are improved sensitivity and accuracy compared with FAAS (30–32, 37, 39, 41, 43, 61, 62). Oil samples have to be pre-treated before the analysis by AAS techniques. Commonly used pre-treatments of oil samples in AAS techniques are dissolution with organic solvents, wet digestion with or without microwave-assistance, and the use of emulsions.

Optical Emission Spectrometers (ICP-OES, LIBS) and Mass Spectrometers (ICP-MS)

In these techniques atomization, and often also ionization and excitation of elements, are carried out by using plasma. Plasma is an ionized gas including also neutral atoms and molecules, and it is macroscopically neutral. The electrical conductivity of the plasma is good and it can be affected using magnetic fields. Potential plasma sources are ICP, direct current plasma (DCP), and microwave induced plasma (MIP). Nowadays ICP is the plasma source mostly used and it is used as an excitation source for both emission and mass spectrometers (ICP-OES and ICP-MS) (76).

In OES techniques the excited atoms and ions produce element-specific emission spectra when the excitation states die. The studied emission line (atom line or ion line) is selected and isolated, and the concentration of the studied element is determined using standard series. Good properties of ICP-OES techniques are the possibility of qualitative analysis, simultaneous analysis (over 70 elements can be measured simultaneously), and wide linear determination range. Furthermore, chemical interferences are minimal and the detection limits are low (76). Although ICP-OES is usually used in metal analyzes of lubricating oils, analysis of non-metals can be achieved as well. For instance, Krengel-Rothensee et al. (77) used ICP-OES in the analysis of Cl, Br, I, S and P in waste oils. Drawbacks of this technique are numerous spectral interferences (that can be avoided with a careful planning of measurements), matrix effects in nebulization and excitation, and the high purchase and operating costs. A very good review of plasma spectrometry was presented by Jarvis and Jarvis in 1992 (78). Their article handles the usage and properties of ICP-OES, DCP-OES and ICP-MS in the analysis of geological and environmental samples. Properties of these methods are presented thoroughly as well as a comparison with other techniques such as the AAS, XRF and NAA techniques. ICP-OES has gained more popularity especially since the mid 1990s. The most typical pre-treatment methods of oil samples with ICP-OES are dissolution with organic solvents, wet digestion with or without microwave-assistance, and emulsification (6, 7, 11, 16, 21, 22, 27, 37, 44, 47–49, 53, 54, 59, 60, 63–65, 71).

ICP-MS uses inductively coupled plasma as an ion source and similar sample introduction techniques as can be applied in the OES techniques. Ions are removed from the plasma into the MS through nickel (or platinum) cones. The MS part isolates different ions and guides them to the detector. Quadrupoles, double-focusing magnetic sector devices and time-of-flight (TOF) devices are used as MS. The mass spectrum is obtained by recording intensity (pulses/second) as a function of mass-to-charge (m/z) ratio. The benefits of the ICP-MS technique are a very wide linear determination range, capability to measure 75 elements, short measurement times, very low detection limits, and the potential for qualitative analysis. The drawbacks of ICP-MS are isobaric and molecular ion interferences, as well as similar matrix effects as in the ICP-OES technique. Furthermore, the purchase and operating costs in the ICP-MS technique are very high. Good reference material on ICP-MS, by Thomas (14), is available in the reference. Bings (79) combined LA with ICP-TOFMS in an analysis of 11 metals in lubricating oils. Oil samples were not required to be decomposed or diluted. The only pre-treatments in this case were the shaking and ultrasonic mixing of heated oil samples. Calibration was carried out using two methods: external calibration with standard oils and aqueous solution-based calibration. Precision and detection limits of this method were good using either of the calibration methods, but stable ablation required modification of the ablation cell and an accurately adjusted laser. Signal stability was not affected by metal or soot particles. Escobar et al. (80) used ICP-MS in the analysis of Al, Mg, Fe and Y in lubricating oils. These metals are critical when detecting wear in Si_3N_4-steel bearing systems. They used electro-thermal vaporization in sample introduction. The determination of magnesium seemed to be the most difficult, because of C_2 interference. The detection efficiency of aqueous elements was higher than that of metallo-organic elements. Boulyga et al. (81) used the isotope dilution (ID) ICP-MS with LA (LA-ICP-IDMS) in the analysis of sulphur in petroleum products (gasoline, diesel, heating oil). LA-ICP-IDMS provided data comparable with microwave digestion and the ICP-IDMS method when certified reference materials were studied. Results of real samples were also otherwise similar, except that a diesel fuel analysis produced slightly different results with LA-ICP-IDMS than with the microwave digestion applying method. The good aspects of using the method are its high accuracy, sensitivity, and short analysis times (~10 minutes). If there is a suitable ^{34}S-spike compound available, then LA-ICP-IDMS has very good potential in becoming a routine sulphur analysis method in the petroleum industry. The isotope dilution technique in the sulphur analysis of gas oils has also been used by Hearn et al. (82). Emulsification and FIA sample introduction (83), microwave digested samples (50), (84), and dilution of oils with organic solvents (23, 28, 29) have also been used as sample pre-treatment methods of oils before ICP-MS measurements.

A very powerful laser beam (Nd:YAG) is used to atomize and/or ionize the sample material in LIBS. Metal atoms and ions are excited and the death of the excitation state causes a characteristic light emission, which can be accurately determined. The power of the laser and the sensitivity of the detector set the limits for this technique. The LIBS technique is very similar to LA sample introduction, and it can even be seen as some kind of a "predecessor" to the LA method. In the LA method, ablated material is directed to inductively coupled plasma, which is used as an excitation source and the determination of elements is carried out by OE or MSs. In LIBS ablated material is immediately heated and a "plasma cloud" is formed. The plasma cloud atomizes/ionizes the sample and excites the metal atoms or ions. When the plasma cools down, characteristic emission lines of elements can be observed. Yaroshchyk et al. (85, 86) used LIBS in the wear metal analysis of motor oils. Calibration was carried out using multi-element standards. Because LIBS does not require complex sample treatment, it might be applied in online monitoring of wear metals in lubricating oils. A drawback of the method is the requirement of large sample volumes (over 80 ml).

An outstanding review article on atomic spectroscopy handling of the techniques presented earlier in this article has been presented by Bings et al. (87) in 2006.

XRF

X-rays are highly energetic electromagnetic waves; their wavelength area is about 0.01–10 nm, and their frequency range is 30–3000 PHz. When an atom is irradiated with a sufficiently large amount of energy, its inner shell electrons may be expelled from the atom. The escaping of electrons causes emptying of an electron orbit, which is filled by outer race electrons. Because outer shell electrons are more energetic than required to fill the empty orbit, the excessive energy is released as X-rays. These X-rays are called secondary radiation and the phenomenon XRF. Each atom radiates a specific emission line when stimulated to do so. Characteristic wavelengths are then used to detect specific elements. Quantitative analysis is carried out by detecting the intensity of the emission. XRF has been used to monitor additive and wear metals in oils, as well as in oil filter analyzes. Lighter elements, such as Mg, Si and Al, can not be monitored while suspended in oil. XRF spectra are relatively simple, hence spectral interferences are rare. The method is non-destructive, the sample amount can be highly variable, the procedure is also fast in the multi-element analysis, and the accuracy and precision of the method are good. The disadvantages of XRF are quite a low sensitivity, difficulties in the analysis of lighter elements, and the relatively expensive instruments (3, 76).

Kubo et al. (88) used XRF in the analysis of fuel and oil shale samples. López et al. (89) determined vanadium, sulphur and nickel concentrations in crude oils using XRF. Ojeda et al. (90) studied the same elements as well as iron in crude oil using XRF. They obtained detection limits of 20 μg/g for sulphur and as low as 0.1 μg/g for iron. The accuracy was 4% when a reference material was analyzed and the reproducibility was 2–6%. Zararsiz et al. (91) compared different sample treatment methods before XRF analysis. These methods were: no sample treatment, pellet forming, and chemical treatment. Chemical treatment was observed to be the most efficient treatment method, and viscosity or high particle concentrations of oils did not cause any problems in the determination after that treatment. Reus (92) also compared different sample preparation methods of oils and greases before XRF analysis. The simple dilution method yielded good results if element concentrations were above 1 μg/g. If the element concentrations were lower, ashing in low temperature oxygen plasma could be recommended. That method made detection limits of only a few ng/g possible. Digestion with nitric acid and an extraction method were observed to be ineffective in this case. Liu et al. (93) proposed a pre-treatment method in which oils were mixed with magnesium oxide, as a result of which pellets were formed. The pellets were analyzed by XRF. The results of V, Cr, Mn, Fe, Ni, Cu and Zn analyzes were accurate and precise indicated by recovery tests and comparison tests with other methods. Limits of detection ranging between 0.6 and 3.8 μg/g were obtained when MgO containing no trace impurities was used. Pouzar et al. (94) did not use any sample pre-treatment, and yet obtained detection limits of 1.20 to 7.11 μg/g and good accuracy, as compared with the ICP-OES analysis. The analyzed metals were Fe, Zn, Pb, Cu and Cr. Yang et al. (95) proposed a particle size-independent method for wear metal analysis in engine oils using an energy dispersive XRF spectrometer. They digested oil samples applying mild nitric acid and microwave-assistance. After digestion 0.5 ml of each sample was spotted onto an extraction disk. In this way, particle size dependence and sedimentation of metal particles did not cause problems. The developed method seemed to be accurate and precise. Detection limits for Fe, Cu, Zn, Pb and Cr were between 1–5 μg/g depending on the metal studied. Recovery experiments, too, gave acceptable results for spiked samples varying between 92 and 110%. The results were also comparable to results achieved in the ICP-OES analysis. One major advantage of the method is that the extraction disks can be easily stored after the analysis for potential extra analyzes. Drobyshev et al. (96) used XRF in the analysis of V, Ni, S, P, Ca, Cl and Pb in oil products. They observed that light elements, and especially sulphur, should be analyzed using a palladium secondary target. Intermediate elements, such as V and Fe, should be analyzed using a molybdenum target, whereas the right target for heavy elements from Mo to Ce is corundum.

Ferrography, Microscopic Techniques and Particle Counters

Ferrographic devices can be roughly divided to direct reading ferrographs (DRF) and devices of analytical ferrography. DRF determine relative concentrations of ferrous particles in size classes of below and above 5 micrometers. These results can be used to calculate total wear particle concentration, or the proportion of large particles. Analytical ferrography can be applied to determining particle types, concentrations, sizes, distributions and morphology. The ferrographic oil analyzer consists of a slide preparation unit and an effective microscope. The studied oil sample is diluted with a fixer solvent and directed over the slide, which is under the influence of a magnetic field. Metal particles precipitate on the slide in a decreasing size order. Ferrous particles form lines parallel to the magnetic field. Non-magnetic metals and non-metals distribute randomly on the whole slide. The slide is studied with a microscope. When the required microscopic information (particle sizes, amounts, types) has been stored, the slide can be heated or treated chemically in order to get metallurgical information on the structure of large particles (3). Different kinds of techniques for the slide preparation and its analysis are proposed in the literature. It is possible to use a rotary particle depositor, in which the slide is rotated and placed on a stationary magnet (4). In 1984 Goldsmith presented a ferrokinetic microscopic stage for ferrography, applying a rotating magnet on the microscope platform as cited by Roylance and Hunt in reference (4). Nowadays analytical ferrography utilizes sophisticated computer analyzes and the Wear Particle Atlases available. Ferrography is always time demanding, the operator has to be experienced, and samples can rarely be used without dilution. On the other hand, ferrography has gained popularity in analysing heavy oils and greases. Studies applying ferrography and development of new techniques related to ferrography are also common these days. A good review article on the development of ferrographic techniques was presented by Roylance in 2005 (97). Myshkin et al. (98) presented an optical ferroanalyzer in 2003. They analyzed the concentration of ferrous particles in lubricants by observing changes in optical radiation. The studied substrate reflects optical radiation on the accumulation areas of large and small particles under the influence of a magnetic field. Variations in the lubricity of oils are detected as changing optical density. Chiou et al. (99) developed an on-line ferrographic analyzer. Their analyzer uses Hall-effect sensors between the poles of a magnet to detect wear particles that are captured in an air gap between the poles of the magnet. Wear particles change the density of the magnetic flux, thus the larger the change, the larger the amount of wear particles. The density of the magnetic flux influences the Hall-effect sensor by causing a difference in the output voltage, as compared to the normal situation without wear debris. Correlation between the voltage difference and the amount of wear debris can be calculated. Ferrographic techniques have also been used in various studies related to wear detection of machines and machine elements, such as gears, combustion engines, steam turbines, hydraulic oil filters, couplings, etc. (100–108).

Microscopic methods can also be used to study wear particles in oils once the particles have been filtered from the oil. Various types of microscopes have been used in studies related to wear detection of machine elements (109–119). Those often used are normal optical microscopy and scanning electron microscopy. When wear debris is studied using microscopy, wear particles are often classified into different groups, which makes the detection of sources of wear and wear mechanisms easier. A classification often used is presented by Roylance and Hunt (4). Wear particles are classified into six classes: rubbing, cutting, laminar, sphere, fatigue, and severe sliding particles.

Optical microscopy is based on the use of visible light and an optical microscope as an instrument that consists of an illumination system, one or more lenses, and accessory optical devices producing enlarged images of an object, which is placed on the focal plane of the lenses. The produced images can be photographed or stored as digital images by applying special equipment. The standard optical microscope is a bright field microscope, which however has certain limitations. Hence, other techniques have been developed in order to better contrast images, such as dark field and fluorescence microscopy, phase-imaging systems, polarization microscopy, and illumination by IR, UV or X-ray radiation. Signals produced by an excited analyte consist of electron beams instead of photons in electron spectroscopy. The analyte is usually excited by monochromatic X-rays, in which case the technique is called electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS). In the Auger electron spectroscopy (AES), excitation is carried out by electrons or X-rays, while UV radiation is the excitation source in UV photoelectron spectroscopy (UPS). We will concentrate especially on the scanning electron microscope (SEM), because it has been used commonly in wear debris analysis. An SEM image is produced by scanning the studied surface (a used oil filter) by a focused electron beam. Different types of signals are produced from the surface: backscattered and secondary electrons, Auger electrons, XRF, and photons with different energies. Backscattered and secondary electrons are the ones mostly used and they form the basis of SEM, whereas XRF is used in the electron microprobe analysis, i.e. in detecting elemental compositions of particles. A combined SEM and electron microprobe analysis device consists of an electron gun, electron optics, a sample chamber, and a detector. The electron gun can be a heated tungsten filament in a high potential, a lanthanum hexaboride rod, or a field emission type cathode. Electron optics has a magnetic condenser and an objective lens system. The condenser guides the electron beam to the objective part, which determines the size of the electron beam that bombards the surface of the sample. Scanning of the surface is carried out by electromagnetic coils controlled by electric signals. As a result, an actual map of the surface is produced. The sample chamber has a very low pressure ($\leq 10^{-4}$ torr), and the sample holder is suitable for sample sizes up to the range of a few centimeters. One should keep in mind that only conducting samples can be studied, hence non-conducting samples are coated with a thin metal layer. Detectors can be either scintillation detectors or semiconductor detectors. The X-rays produced can be observed by an energy or wavelength dispersive spectrometer (EDS/WDS); modern systems including both of them (3, 4, 76, 120).

Particle counting methods do not distinguish between qualities of solid particles, but they can detect wear metal particles, too. Particle counting can be carried out manually using an optical microscope, but this requires quite a bit of time and expertise. Nowadays there are a lot of commercially available automatic particle counters. They are available for continuous on-line monitoring, and also as portable and laboratory devices. The majority of modern particle counting techniques are based on optical measurements. The basic principle of optical particle counting is the blockage of light. A light beam is directed through an oil sample onto a detector. When the beam hits an opaque particle, an amount of light proportional to the size of the particle is blocked. This causes a change in the electrical signal at the detector. The change is subsequently compared against calibration of the device, hence producing the particle size and count as a result. What is ultimately determined are particle size distributions as ISO cleanliness values or alternatively, various distributions calibrated by the user. Light blockage counters are affected by fluid opacity, air bubbles and water. In addition, highly viscous fluids or fluids containing very large amounts of particles may be difficult to measure. On in-line devices usually have a limited amount of measurement channels and other functions, thus making them relatively cheap. Alternatively, sophisticated laboratory devices may have dozens of measurement channels and a possibility to eliminate the influence of water and air. Other types of particle counters are based, for example, on flow decay or mesh obscuration. Flow decay counters use calibrated mono-size micro sieves. Samples are then compared with a well-known standard. Mesh obscuration counters are based on a pressure difference caused by particles blocking micro-screens of three different pore sizes in the instrument. The count data is calculated from the correlation of unknown samples and the calibration standard. Mesh obscuration counters are more reliable than flow decay counters. They are effective even for black oils, and are usually not affected by water or air bubbles. Particle counters can be applied in the condition monitoring of various types of oils, such as hydraulic oils, rolling oils, gear oils, etc. (3, 4, 110, 121–127).

Chromatographic Techniques

Chromatographic techniques are based on the interactions of components of the studied samples between the mobile and the stationary phases of the instrument used. The mobile phase can involve either a gas, a liquid or a supercritical fluid. Stationary phases are placed in a column or stand on a solid support material. Components of the sample that have a strong interaction with the stationary phase tend to move slowly through the column, and separation of the analytes occurs. Chromatographic methods produce chromatograms as a result. The chromatogram presents the determined signal as a function of time, while points of different peaks in the chromatogram help to identify components of the sample; the areas or heights of the peaks can be used in the quantitative analysis. The most commonly used techniques in oil analysis are liquid chromatography (LC) and gas chromatography (GC) (76).

The performance of LC is affected by the column (its resolution, capacity, selectivity and temperature), the flow rate of the eluent (mobile phase) and the rate of sample injection. LC is divided into different groups regarding the stationary phase used and the separation mechanism. The most commonly used HPLC uses high pressure to force the eluent to move through packed columns. When the stationary phase is more polar than the mobile phase, the technique is called normal phase (NP) LC, whereas in the opposite situation the technique is known as reverse phase (RP) LC. NP-HPLC uses silica-based columns with aluminium oxide and polar phases, such as cyano-, amino-, diol- and nitro groups attached. Eluents are more often rather non-polar, for example, hexane, chloroform or ethyl ether. RP-HPLC uses mixtures of water and, for example, methanol, acetonitrile or tetrahydrofurane as eluents. Stationary phases are usually C_{18}, C_8, C_2 or phenyl compounds attached to silica. UV, UV-visible (Vis), fluorescence, electrochemical and refraction index detectors are used with LC. In addition, infrared spectrometers and MSs have also been used as detectors with LC (76).

In the GC technique, samples are vaporized and injected to the column. In the mobile phase an inert gas (helium, argon, neon, carbon dioxide or hydrogen) is applied, which is selected based according to which detector is used. The mobile phase does not have an interaction with the analyte molecules. The stationary phase is placed on a column which can be a packed or an open tubular/capillary type. Open tubular columns are more efficient than packed columns; currently the most commonly used columns are fused-silica-type open tubular columns. Stationary phases can be modified based on the studied analytes, thus phases can be highly polar (polyesters), polar (cyano or hydroxyl groups), or non-polar (dialkylsiloxanes). In addition to the column, a very significant variable is the temperature used, which should be above the boiling point of the studied substance. If mixtures with wide boiling point ranges are studied, temperature programming of the GC oven should be used. Flame ionization, thermal conductivity, thermionic, electron capture, atomic emission, flame photometric and photoionization detectors can be used with GC. A gas chromatograph can also be attached to a MS or an infrared spectrometer (76).

Khuhawar et al. (67, 68) analyzed vanadium, copper, nickel and iron as metal complexes in crude oil using HPLC. They used both NP-HPLC and RP-HPLC. The applied eluents were a mixture of 1,2-dichloroethane, chloroform and acetonitrile and a mixture of methanol, acetonitrile and water. The column materials used were silica and Microsorb C_{18}. The results of both studies were good. Salar et al. (128) determined the same metals in crude oils using 8-hydroxyquinoline in acidic media as an extraction solvent. The applied eluent was a mixture of methanol and water, and a RP C_{18} column was used in the HPLC analysis. V, Ni and Fe were determined in crude oils using HPLC by Tadayon et al. (129). Khuhawar et al. (130) also used HPLC in the analysis of vanadium in petroleum oils using 2-acetylpyridine-4-phenyl-3-thiosemicarbazone for derivatization. Habboush et al. (131) developed a direct solvent extraction-gas chromatographic method for determining organophosphorus additives in engine oils. They used ethanol as an extractant, nitrogen as a carrier gas, and a 3% OV-17 (50% phenylmethylpolysiloxane) column. Ethanol was a good extraction solvent because its polarity is high and it extracts polar organophosphorus additives well. It is also not toxic and easy to work with. When different engine oils were spiked with typical organophosphorus additives (triphenylphosphate and *p*-tricresylphosphate), errors ranged between 0.70–2.80%, and 0.40–2.96% in the analysis of the mentioned additives. RSD values were 2.4 and 2.8% at the maximum. Hence, the developed method proved to be accurate and reliable, as well as relatively fast (the analysis time of one sample was 20 minutes). Lambropoulous et al. (132) used HPLC to separate zinc dialkyldithiophosphates as zinc complexes from lubricating oils. They used a silica column and two kinds of eluents: A) isopropylamine-acetic acid-methanol in dichloromethane and B) isopropylamine-acetic acid-methanol in n-heptane-dichloromethane. Becchi et al. (133) used pentafluorobenzyl ester derivatives to identify zinc dialkyl- and diaryldithiophosphates in engine oils using the GC-MS technique.

Neutron Activation Analysis (NAA)

NAA is based on detecting different elements according to the gamma rays they emit after neutron activation. Nuclear reactors, radionuclides and accelerators are used as neutron sources. Nuclear reactors usually produce thermal neutrons (energy about 0.04 eV) with high neutron densities. Radioactive isotopes are suitable and moderately cheap neutron sources, albeit the achieved detection limits for the elements studied are weaker than with the reactor technique. Accelerators produce high-energetic neutrons (14 MeV), which are required to activate certain lighter elements. Activation methods can be destructive or non-destructive. Both the studied sample and the standards are activated simultaneously by neutrons. The exposure time and neutron flux should be similar with both the standards and the samples. Irradiation can last from minutes to hours, based on the nature of the samples. After irradiation, samples and standards are allowed to decay in the so-called cooling period, which can last from minutes to several hours or more. The radioisotopes subsequently emit gamma rays and energy. The released radiation is element-specific: over 70 different elements can be detected. The difference of non-destructing or destructing methods is related to the counting stage of gamma rays. Gamma rays are detected right after the cooling stage in non-destructing methods, and the spectrometer should have a good resolution. The studied analyte is separated from other components in destructive methods, and only the amount of gamma rays produced by the separated analyte is detected. One of the main benefits of the NAA technique is its minimum requirements for sample treatment; the only treatment required is usually weighing the right amount of sample into the sample vessel. The NAA technique also has high sensitivity and good accuracy, and it is easy to calibrate if standards similar with the samples are available. NAA is also a very good reference technique for atomic spectroscopic techniques, because its basic functioning principle is totally different than in the atomic spectroscopy (134). The drawbacks of this technique are long analyzing times and expensive equipment including radioactive material (76). NAA was used for determining metals in oils in 1970 by Flaherty and Elridge (135). Adeymo et al. (136) used NAA for analyzing altogether 18 trace elements in crude oils. Elements in crude and lubricating oils have been analyzed by NAA also by El-Dine et al. (137) and Cam et al. (138). Obi et al. (139) and Soliman and Zikovsky (140) analyzed different vegetable-based oils using NAA. Owrang et al. (141) applied the cyclic fast NAA in the study of oxidation of mineral and synthetic-based engine oils. Other application areas of NAA related to oils are studies on various fuels, such as coal, fuel oil, gas oil and oil shales (142, 143). NAA can also be used to determine elements otherwise difficult to analyze in oils, such as oxygen and nitrogen (144, 145).

CONCLUSIONS

This article combines all common wear metal analysis techniques and different pre-treatment methods of oil samples prior to wear metal analysis. The pre-treatment methods discussed are: no pre-treatment, dissolution with organic solvents, ashing, wet digestion with or without microwave-assistance, the use of oil emulsions, the use of complexing agents, and acid extraction. The measurement techniques discussed are: AAS, OES, MS, XRF spectroscopy, ferrography, microscopy, particle counting, chromatographic techniques, and NAA.

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