



X-Ray Methods for Monitoring Machinery Condition

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ABSTRACT

As machines operate, particles are removed from the contact surfaces and may be carried away in the flow of lubricating oil. It has been common practice for several decades^{1,2} to analyze lubricating oils in order to identify the wear metals present, quantify them in terms of machine component wear, and to use that information to perform maintenance based on the condition of the machine rather than simply scheduling costly overhauls when they may not be needed. X-ray fluorescence analysis (XRF) is a powerful tool for elemental analysis of structural metals, and is suitable for determining wear metal quantity, elemental composition, production rates for each element, and wear sources. This paper will briefly review the x-ray related techniques which have been used to study or monitor the wear condition of machinery, with a particular regard to Navy interests.³

INTRODUCTION

Wear particle analysis seeks to determine the quantity of worn material, the composition of the wear debris, the source of the wear debris, the wear rate of each source, and the wear mode or manner in which the debris was mechanically produced. The total quantity of wear debris in a drawn oil sample is the most easily determined quantity, but is insufficiently informative unless trends in the quantity are correlated with the progression of machine wear. Wear modes are subjectively assigned by a skilled microscopist based on the shape of individual particles (e.g., lathe turnings arise from a different wear mode than particles removed by spalling).

The most valuable information is the identification of wear sources and their wear rates, since these factors identify whether and where maintenance is to be performed. The most comprehensive profile of sources and production rates of wear metals and particulate contaminants arises from comparing the results of quantitative elemental analysis with the known metallurgy of the machine.

WEAR PARTICLE ANALYSIS METHODS

Two x-ray methods have proven useful for the quantitative elemental analysis of wear debris. These are XRF and the use of a scanning electron microscope (SEM) equipped to perform x-ray

emission spectroscopy (XES), a method referred to here as SEM-XES. SEM-XES is applied to clean, conductive, individual particles, typically while the particle morphology is being examined⁴ for wear mode indicators. The focused beam of high energy electrons of the SEM excites the particle to emit a spectrum of x-rays at energies characteristic of its constituent elements. Selective photon detection at the characteristic energy of a given element, in synchronism with raster scanning of the sample by the SEM, permits viewing the particle as a concentration map image of that element. Despite the power of this technique for identifying the source of an individual particle by determining its alloy, its high costs (facility, equipment, labor, sample preparation, data analysis) in comparison with other methods make it unsuitable for routine monitoring of machine condition. Wear rate information can only be determined in the SEM by laborious counting of many particles of like composition.

X-ray fluorescence analysis (XRF) is a well established, convenient method for quantitative elemental compositional analysis of solids and liquids. Rather than use electrons to stimulate the sample characteristic x-rays as in SEM-XES, XRF applies an incident x-ray beam. The resulting x-ray spectrum is emitted immediately by the sample, and is called fluorescence. As applied to wear debris samples composed of collections of particles, XRF provides wear rate and wear source information based on the composition of the entire debris sample. XRF has been applied to wear debris samples still suspended in the oil as well as to debris separated from the oil.⁵

Wear particle analysis methods not involving x-rays are discussed by Toms.² For several decades, the use of optical atomic spectroscopy (atomic emission spectroscopy (AES), as well as its predecessor as a field monitoring method, atomic absorption spectroscopy (AAS)) has been the substance of military aviation's Spectroscopic Oil Analysis Program (SOAP). AES selects a small volume (μl) of oil from a drawn sample (several ml), momentarily raises it to flame temperatures, and measures the emitted light at preset optical wavelengths characteristic of the elements of interest. All of the wear metal limits in the SOAP were generated from the AES analysis of oil samples. Thus, AES is the benchmark analytical technique to which all others must be compared. AES and AAS suffer from a well-documented particle size limitation^{4,6} in being unable to analyze particles $\geq 10 \mu\text{m}$. Particles $\geq 10 \mu\text{m}$ ("well in excess of $5 \mu\text{m}$ "⁷) are important indicators of wear.

XRF, being a mass sensitive technique, does not have particle size cutoffs, and can be used to measure particles of any size. While there does exist a well known particle size effect for XRF,⁸ it is concerned with efficiency and the details of quantitation.⁹ The sensitivity of XRF (x-ray counts per gram) is highest for small particles (≤ 1 micron). The sensitivity of XRF to larger particles is less than for the small particles. That is, XRF benefits from high sensitivity from small particles which likely are present in smaller total mass. The more massive large particles, despite their comparative inefficiency at producing x-rays, still yield sizeable total signals. Thus, XRF measures both small and large particles.

The particle size effect has to do with particle thickness. Signal level does increase as particle thickness increases, but for large particles (thicker than $\sim 10 \mu\text{m}$ for most metals) it saturates at the signal level of a bulk sample.⁵ Further increases in thickness yield essentially no additional signal.

Cumming and McDonald have found particle size to have only a minority effect on the XRF analysis of wear particles in real and modeled oil samples,¹⁰ although larger effects apply in some cases.⁸ XRF has been observed to be up to fifty times more sensitive than atomic spectroscopy for real samples¹¹ containing large particles. Comparisons of XRF, atomic spectroscopy,¹² and size-independent chemical measurements (involving acid digestion^{4, 13, 14}) show that the XRF results are validated,¹⁰ even where atomic spectroscopy falls short.^{11, 15} Acid digestion¹⁶ as well as grinding¹⁷ of wear particulates have been performed in conjunction with XRF to avoid particle size influences, but the preferred method is to address the issue mathematically.⁹ Where the possible presence of large particles was not of concern, thermal degradation of the oil has been used to preconcentrate the metals into pellets in preparation for analysis by XRF.¹⁸

Both AES⁴ and XRF are susceptible to matrix effects, wherein the presence of one element influences the emission of another. For AES, organometallic reference standards comprised of fluids closely comparable to the sample must be kept on hand. The XRF matrix effect in homogeneous samples can be treated by computation alone. XRF measurements of organometallic standards compare well with atomic spectroscopy. However, XRF can calibrate adequately with a single solid reference standard. The XRF matrix effects for thin layer samples on a membrane filter are largely limited to effects within a given particle, with a small contribution from nearest neighbor particles. Comparative analyses of wear particulates, conducted by XRF and by chemical methods independent of particle size, referenced above, have shown good agreement, despite the fact that samples composed of mixed particulates cannot be considered homogeneous.

The detection limits required to warn of an impending failure vary widely from one machine type to another. For one type of turbine engine, Fe at a few ppm (parts per million) is acceptable but 15-20 ppm Fe in oil requires maintenance.¹⁹ Typical detection limits and precision required²⁰ for AES instruments are 1 ppm. Detection limits for XRF are subject to many factors, but the ability to detect ppm concentrations in bulk samples is common.^{5, 21} Gilfrich has gathered detection limit data from a number of sources, and normalized them to a 100 sec counting period.²² He reports that 0.1 ppm is the best achievable in bulk samples, but that, for thin samples having reduced backgrounds, detection limits can be improved 1000 times beyond that, typically below 25 ng/cm² on a thin filter. These levels are well below that required for condition monitoring of typical wear debris samples.

Energy dispersive XRF (EDXRF) instrumentation⁵ is robust, not sensitive to alignment, and offers the ability to measure multiple elements simultaneously with a single, readily calibrated energy dispersive detector. Although XRF cannot perform the required analyses for light elements such as Mg, Al, and Si while the particulates remain suspended in oil, this difficulty is removed by filtration.

The relative merits of fluid samples and separated particulate XRF samples should be clearly delineated. The main advantage of fluid analysis is the simplicity of sample preparation and availability of the result as a concentration in ppm. Particle separation is conveniently performed by filtration, and the analysis then falls within the category of filter debris analysis (FDA). The depth filters used on oil lines are not suitable as XRF sample filters, as the particulates are buried in the filter media resulting in x-ray absorption problems. Membrane filters are better suited to x-ray

analysis. Separation from the oil avoids (1) x-ray backscatter from the fluid, (2) fluorescence from the fluid, (3) particle settling, (4) x-ray absorption by the fluid. Further, separation effects a pre-concentration of the particulate sample. Low atomic numbers (Mg, Al, Si), whose fluorescence would be absorbed by oil, may be separated on the filter, placed within a vacuum x-ray path, and measured. For best results, to avoid one particle occluding another, the particulates should be displayed to the XRF instrument in a single layer.

STUDIES BY RELATED X-RAY METHODS

Lubrication and tribology have been studied by x-ray photoelectron spectroscopy (XPS), in which an x-ray stimulates electron emission; the electron becomes a surface probe.²³ Bertin found that standard laboratory sources were not adequate for wear particle monitoring by x-ray absorption.²⁴ Proton-induced x-ray excitation (PIXE) has been carried out on metal atoms in oil slicks, to identify the oil's source.²⁵ The material transfer between dissimilar, unlubricated contact surfaces has been studied by XRF.²⁶

Photon emissions at x-ray wavelengths can also be produced by nuclear capture of a K electron. Studies have been performed on nuclear activation of the original machine parts,²⁷ as well as of the collected, active wear debris.²⁸ Gamma rays have also been used to monitor wear by placing the detector near the machine and measuring the decrease in signal as the radioactive surfaces abrade away. Or, the active particles may be measured while remaining in the oil (the gamma rays being sufficiently penetrating to escape the oil), whether in a drawn sample or while still circulating.²⁷ Separated wear particulates must be suitably introduced into the scintillation liquid, which may involve acid digestion and other steps. Other workers filter the inactive debris and then neutron irradiate the particles and perform quantitative instrumental neutron activation analysis (INAA) for as many as 19 elements. This non-destructive method has been found to offer higher detection sensitivity than AES, while yielding similar quantitative results for turbine engine samples.²⁹ The gamma ray methods are insensitive to sample form or particle size because of the high photon energies measured, but are not suitable as a routine maintenance monitor for a variety of reasons, principally relating to radiation safety, handling, and costs of labor and facilities.

XRF STUDIES OF WEAR DEBRIS

A sampling of XRF studies of wear metals since the early 1970s begins with the analysis of wear particulates suspended in oil.²⁴ In 1974, Harman reported an Oil Debris Monitor (ODM) for detecting metal in recirculating lubricating systems by XRF, with the intended goal of in-flight use.³⁰ A 30 millicurie plutonium (Pu^{238}) x-ray source and an Ar- CO_2 proportional counter with a 250 μm Be window monitored for dissolved and suspended ($<300 \mu\text{m}$ test spheres) Fe in oil. Reported performance was 0-550 ppm with accuracy ≤ 6 ppm. Counting times were 4-60 minutes (~10 minutes typically), to be compared with engine oil flow rates of 4-60 liters/minute. The Pu^{238} source, with a biological retention half-life of 200 years (radiative half-life 86 years), was chosen once it was determined to be 2000 times more effective as an x-ray source than the preferred chemically unreactive Kr^{85} source, for which the biological half-life is but 0.01 year. Mixed results accompanied

attempts at introducing large Fe particles into the oil as calibrants. The major outstanding issue was the fragility of the gas proportional counter, which was subject to uncontrollable aging and premature mortality without warning.

A similar on-line monitor with a 10 minute measuring time was reported^{19, 31} by Miner and Packer. An attempt to monitor suspended Fe particulates in the lab did not succeed, and was not attempted on the engine test stand. X-ray spectral resolution was heavily degraded by engine vibration (30% broadening & lowering from 7000 rpm to 9200 rpm).

The 1979 work of H. Meier, et al.,³² reports XRF for early damage detection in diesel motors and bearings, and is notable for its breadth in terms of sources, detectors, and sample forms used, both in calibrations and in studies of operating machinery. Various primary radionuclide sources were employed in point and ring geometries. A miniature x-ray tube used a metal scatterer/converter as a photon energy selector. Single and dual channel analysis with x-ray filters in the beam were demonstrated as simple, lower cost competitors to EDXRF for particular cases, although its performance was admittedly not as good. Calibration curves were taken for fluid samples and for thin layer, filtered samples, for the common metals encountered in the diesel motors (Fe, Cr, Cu, Ni, Zn, Pb). For fluid samples, detection limits with radionuclide sources were 5-20 ppm of dissolved metal, while the W-anode x-ray tube with metal converter offered 1.5 ppm detection of Fe in oil, and somewhat higher for other metals of interest. Comparisons to AAS were made, which were linear passing through zero, but with the AAS reading about 25% higher for unexplained reasons. Detection limits for thin layer samples were 2-10 µg/filter, or <1 ppm for 10 ml samples, typically performed by these authors with a radionuclide source and any of various detection schemes, the most capable and versatile being the Si(Li) detector with MCA.

Meier, et al., demonstrated the ability to use either dissolved metal or filtered metal particles to perform trending of engine wear. They found, in a diesel engine operating with the usual in-line motor oil filter, that the circulating dissolved Fe metal (i.e., not caught by either motor filter or drawn sample filter on the bench) in the 10 ml samples was 10-20 times more abundant than the residual particles filtered from those samples by 0.6 µm sample filters. Meier did not measure the wear debris retained by the motor filter, whose filtration characteristics were not identified. In one series of measurements, both dissolved and particulate metals showed an expected drop immediately after an oil change, but both showed an unexplained episodic increase which remained in the oil circuit only 150 miles; otherwise, the dissolved metal steadily rose in concentration over 3500 km of operation. In bearing test stands, the in-line oil filter was removed and the particles allowed to continue to circulate, be ground into smaller particles by the bearings, and be included in the oil samples drawn. Under these conditions, the amount of particulate collected was demonstrated, for Fe and other metals, to follow the form

$$V = a \cdot t^b$$

where V is the rate of particle generation, t is time, and a and b are constants. Results for several bearings were plotted out to 60 hours or less, but two went to nearly 800 hours.

One of the most remarkable and compelling results of Meier, et al., was the direct measurement of wear rate ($\mu\text{g/h Fe}$) of a bearing as a function of load, determined by measurement of filtered particles from 10 ml samples by a Cd^{109} XRF system. The load was removed following an oil change, and the wear rate plummeted by nearly two orders of magnitude, then resumed as the load was reapplied (see Meier's Fig. 54).³²

In 1980, Veinot published an important study of wear particulate analysis of samples taken from operational helicopter engines.¹¹ Veinot compared XRF to AAS for monitoring Fe and Cu by measuring the dissolved material and suspended particulates in the liquid oil. XRF showed higher levels of wear metal contamination than AAS. XRF calibration was validated in all cases as determined by ashing, acid digestion, and wet chemical analysis. AAS was less accurate than XRF, especially at high concentrations. XRF indicated an earlier and greater rise in concentration than AAS, as a function of engine operating time. As a result, XRF enabled the onset of failure to be noticed at least one sampling period (~ 20 h) earlier, increasing the likelihood of preventing an unchecked failure. XRF did not saturate at high concentrations, while AAS did. Veinot's data, published in tabular form, are presented below as a 3 dimensional chart, with one set of traces per engine. The AAS trace is always considerably lower than the XRF trace. The full range of Veinot's XRF data has been clipped to 1/3 height to avoid further compressing the AAS plots. Clearly, the XRF analysis offers wider dynamic range and stronger warning than does AAS.

By 1983, B.C. Clark, et al.,³³ were testing a suitcase-portable XRF instrument (OWAX, or Oil Wearmetal Analysis by X-ray) for filtering particles and analyzing them. The fielded OWAX used a gas proportional counter (optional Si(Li)) to analyze for Ti, Cr, Fe, Cu and Zn simultaneously, with ppm sensitivity. The analyte, semi-automatically processed to the form of trapped metal particles and sludge, was extracted from undocumented oil samples drawn from aircraft. Total sample processing and analysis time was under 500 s. Although calibration was done with suspended $1 \mu\text{m}$ Fe spheres, correlation with SOAP was reportedly weak, despite the suitability of this size range to both XRF and SOAP.

The use of single element, wavelength dispersive XRF (WDXRF) for Fe wear particles suspended in oil was reported in 1985 by G. Cumming and I. G. McDonald,¹⁰ who sought to determine the method's accuracy and examine the importance of particle size effects. Truck and test rig oil samples were analyzed for Fe concentrations ranging from 1 to 1200 ppm, with standard deviations of 1%. A wet ashing and acid digestion method of sample preparation for AAS (acid digestion AAS) provided accurate concentrations of total metals in agreement with NBS standards; this method also agreed with XRF to within 14% in all cases, and generally to within 7%. The authors performed theoretical calculations of Fe signal from well suspended large particles compared to the same mass of smaller particles. Even for $20 \mu\text{m}$ elliptical platelets (randomly oriented), they found that the particle size effect is still a minority one. They also noted that, as the large particles settle over a period of hours, the XRF signal can actually increase several times, surpassing that of a suspension of small particles. The settling issue was addressed by Searle and Thompson³⁴ by converting the oil to a grease, but the preferred approach would be to analyze the elements in parallel by EDXRF. Cumming and McDonald concluded that XRF proved to be an accurate, reproducible method for

Helicopter Engine Wear

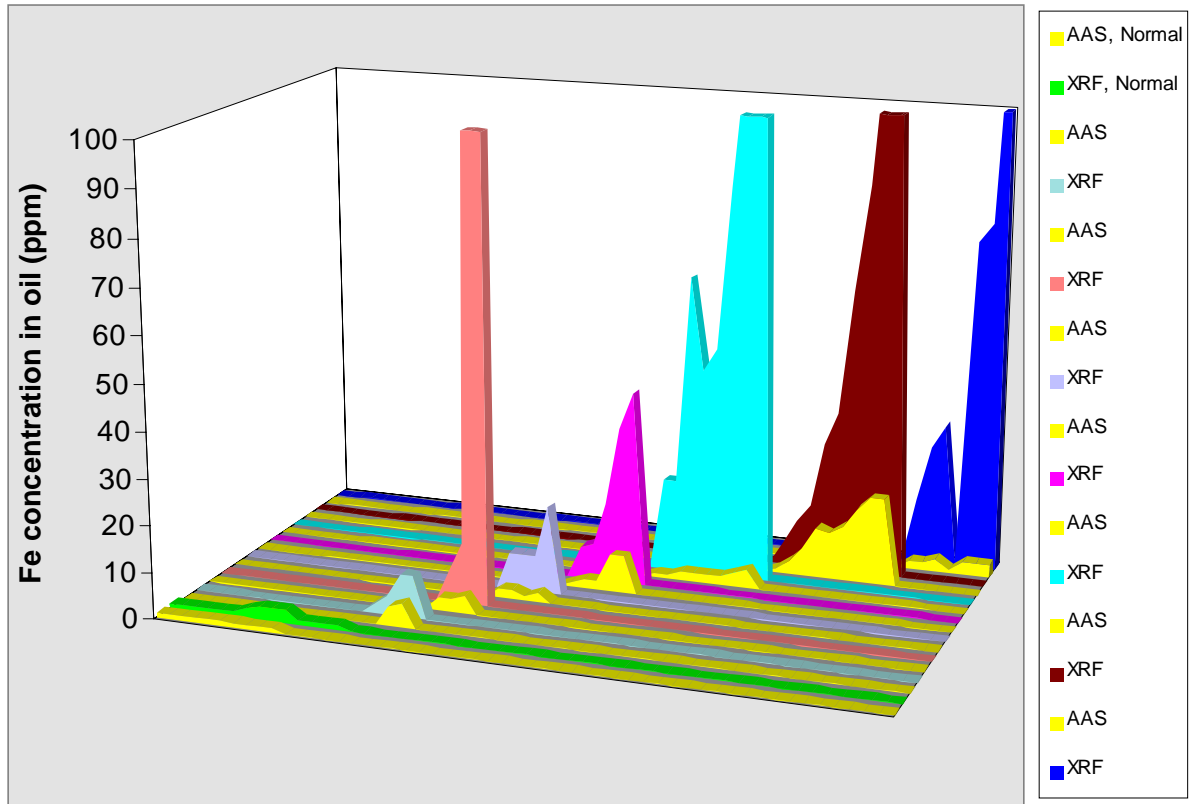


Figure 1. Concentration of suspended Fe in engine oil from Sea King helicopters¹¹ versus engine time (left to right axis, 200 hr range) versus engine (front to back axis, 8 engines). Each data point represents a drawn oil sample which was analyzed by both XRF and AAS. Sampling interval was ~15 engine hours. The direct AAS analysis (yellow traces) is plotted with the XRF analysis (colored traces) of the same sample. The AAS trace closest to the origin and its companion green XRF trace are for an engine with normal wear. The remaining traces are for engines with abnormal wear.

determining Fe in oil, and without the serious particle size effects of either chip detectors or optical spectroscopic oil analysis.

A wider, more in-depth XRF study of real samples of wear particulates recovered from 189 spent lubricating oil filters from a population of F404 turbine aircraft engines has recently been undertaken by Humphrey of the military Joint Oil Analysis Program Technical Support Center.³ The particulates were extracted from the filter medium in an ordinary ultrasonic bath containing a solvent not encumbered by special disposal requirements. A membrane filter separated the particulates from the solvent in a form suitable for introduction to a Spectrace XRF unit having a programmable, multi-

target x-ray tube. EDXRF data for nearly two dozen elements were statistically analyzed and then compared with engine metallurgy and aircraft maintenance records. These comparisons enabled Humphrey to identify wear sources, down to the engine module level. In the case of the lubrication pump bearing, identification could be made to the component level. Corrosion products not normally detected could also be identified by source. Engines which had abnormally high XRF signals for particular metals were also engines which the maintenance database identified as having high engine time, failure, or foreign object damage. A definite signature for these abnormal wear conditions was established, based on the statistics of the population. There were several cases in which filters were analyzed from the same engine at different times, culminating in failure or a high wear condition. Warning of the impending abnormal condition was discernible in the XRF signatures well before actual failure, in some cases in excess of 100 hours in advance.

SUMMARY

X-ray fluorescence analysis (XRF) offers a convenient and robust method for elemental analysis of wear particulates. To gain the highest sensitivities and access the widest range of atomic numbers, it is advisable to remove the particulates from the oil and perform the analysis in vacuum. Since particles thicker than $\sim 1 \mu\text{m}$ undergo significant x-ray absorption, samples of separated particles should be prepared as a single layer. There is a well known particle size effect for XRF, whereby particles smaller than, or layers thinner than, a few μm are measured with greater mass sensitivity than thicker sizes. XRF is sensitive to large as well as small particles. Quantitative comparisons of the elemental analysis of actual wear particulates, performed by XRF and by wet chemical methods independent of particle size, have verified the accuracy of XRF for measuring samples composed of real wear particulates, while highlighting deficiencies in other analytical methods in wide use. XRF has successfully performed the trending of wear rates, identification of wear chemical elements in the wear particles, and location of wear sources. XRF has been shown to be capable of issuing a failure warning over 100 hours in advance. XRF monitoring offers an unprecedented opportunity to achieve significant improvements in the management of machine maintenance and operations, both for the Navy and for industry.

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