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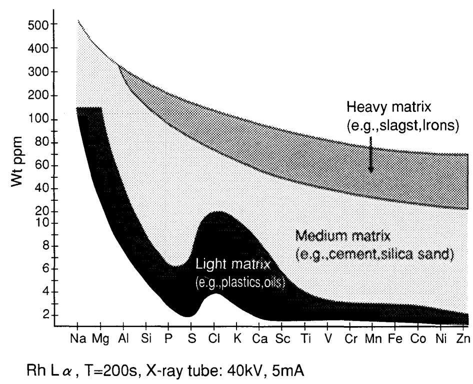
Energy dispersive X-ray fluorescence (EDXRF) spectroscopy is now a well established analytical technique which is applied to elemental analysis. It can trace its roots to developments in the 1960's. Follwing this understanding of the general principles, the first commercial instruments were introduced in the 1970's. Throughout the 1980's and 1990's this technology has evolved through the use of improved components and the implementation of computer technology. The result is an ever improving offering of products which provide customers superior value for their money. There has also been an ever increasing number of applications which have adopted this technology. For a comprehensive review of new technological develpments in this erea, Reference1 should be consulted.

Some of the popularity of this approach relates to its great versatility. It can be applied to both laboratory and on-line quality control types of analysis. In general, the samples require no treatment prior to analysis of the product. The ruggedness of the instrumentation and the ease of operation allow the technique to be used in routine process type applications. The training requirements for operators is now so simple that spectroscopists are no longer required for routine analysis. These very positive features make it a very attractive technique, especially for routine trace level analysis.

A critical area of concern is the lower limit of detection for various elements in different matrices. Since samples comprised of solids, powders or liquids may be analyzed, this issur is critical to consider. The lower limit of quantitation is drastically affected by the material surrounding the element of interest. This effects is dramatically illustrated in Fig.1[2].



Rh Lα, T=200s, X-ray tube: 40kV, 5mA

Fig.1 Typical detection limits for various elements[2]

As can be readily seen, the determination of all the elements are strongly affected by the matrix in which they are present. Also, the lighter elements are much more difficult to measure than the heavier ones. These two trends must be kept in mind when the use of EDXRF is contemplated. It has been the key driving force in limiting the use of this technique in trace analysis.

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Within these inherent limitations, a wide variety of applications have been developed. These span a broad spectrum of industries and are used to solve very specific problems. Some examples would include chlorine measurement in transformer oil to determine PCB contamination. Wear metals analysis in used oil is often measured to determine engine wear in mechanical devices. Another area is the determination of various coating material thicknesses to ascertain the final performance properties of the substrate. Finally, various additive concentrations for formulated food products can be determined to predict the taste and dietary characteristics of the food. These and countless other measurements are routinely performed by EDXRF.

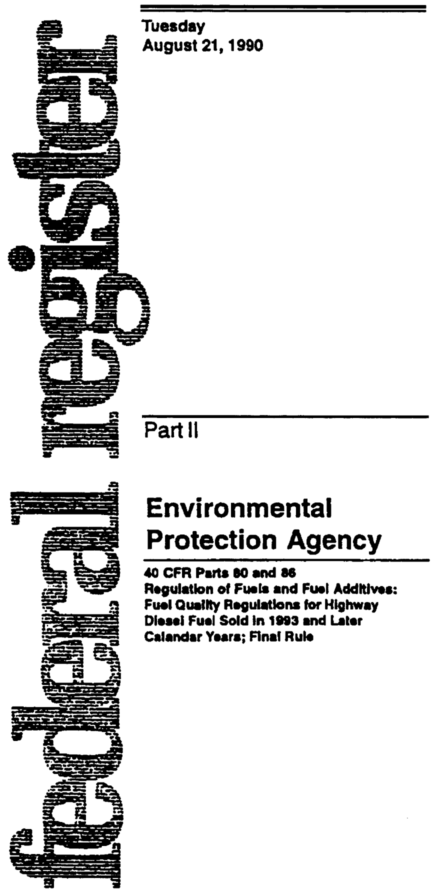
One of the most profound trends has been the development of instruments dedicated to a specific application. In the past, a general instrument was developed and minor modifications, typically in software, were made for specific samples. This approach certainly maximizes the use of the instrument, but the trade-offs may be unacceptable for the customer. This realization has led to the design of the instrumentation customized for the problem of interest. A typical example is the measurement of sulfur in petroleum products. General purpose instruments to perform this analysis have been around for some time, but within the last year most major U.S. suppliers have introduced new products devoted to this market. This has been the method to make the products acceptable to customers.

Another area of change has been the source of energy to cause the excitation. Traditionally the X-rays were produced by a radioactive isotope source. These are reasonably inexpensive and the selection of 3 or 4 key isotopes allows a user to analyze a large percentage of periodic table. This flexibility was critical to handling the variety of applications normally encountered. The move to more dedicated types of analyzers has made it easier to select very distinct characteristics for the source. This has permitted X-ray tubes to be designed and manufactured to tight tolerances to meet the specific application requirements. The inherent safety and ease of use of these tubes suggests that this trend will continue into the future. Most major instrument manufacturers now have X-ray tube devices available.

As the interest in trace element analysis has increased, so has the need for more powerful X-ray tubes. Analysis by wavelength dispersive X-ray fluorescence (WDXRF) analyzers has always been marked by the use of tubes with power levels of several thousand watts. The area of EDXRF is now adopting a similar type of strategy. A generally accepted barrier of 500 watts has been used as the separation of low wattage versus high wattage. Most of the EDXRF units are still in the low wattage regime, but they are beginning to approach high wattage. This trend is expected to continue as lower and lower levels of elements become to interest to potential users.

As the preceding trends have evolved, one of the results has been that EDXRF instruments have been able to displace WDXRF instruments in many areas. The primary benefit of reduced cost (typically 10-20% the cost of a WDXRF instrument)has been the primary driving force behind this shift. However, many of the previously mentioned benefits of EDXRF also apply in comparison to WDXRF. A critical consideration is the ease of use of EDXRF instruments. This leads to faster analysis, less operator training, reduced service and maintenance requirements and lower cost persample analyzed. These benefits will continue to drive the routine analysis of well defined elements in uniform samples to be done by EDXRF.

An example of this trend is the EPA implementation of the 1990 Clean Air Act. Part of this law required that the sulfur level permitted in diesel fuel be reduced to 500 ppm's. The implementation, which was promulgated in 1990, is shown in Fig.2. In this ruling the EPA established ASTM Procedure D2622 (WDXRF instrumentation) as the referee procedure for measurement. However, ASTM Procedure D4294 (EDXRF instrumentation) was accepted as an alternative under controlled operating conditions. This concession to a pragmatic solution is being adopted in an increasing number to industries.


federal register

Tuesday
August 21, 1990

Part II

Environmental Protection Agency

40 CFR Parts 80 and 86
Regulation of Fuels and Fuel Additives: Fuel Quality Regulations for Highway Diesel Fuel Sold in 1993 and Later Calendar Years; Final Rule

Fig.2 EPA regulations for fuels and fuel additives

This example of the determination of sulfur content of petroleum products can also be applied to the other trends previously discussed. This industry is confronted by some perplexing problems which EDXRF is well suited to analyzing. One of the overriding problems is that sweet crude oil is becoming harder to find for subsequent processing. This trend is shown in Fig.3[3]. It is very clear that the average sulfur level is increasing worldwide. Especially in the case of U.S. crude, it is increasing dramatically. Thus, there is a strong drive to be able to accurately measure the sulfur at the percentage level. The cut-off point between sweet and sour crude (0.5wt%) is especially critical to measure accurately. These high sulfur levels are easily analyzed on current EDXRF instruments.

On the other side of the coin, environmental regulation organizations throughout the world are requiring lower and lower levels of sulfur in the finished petroleum products. This trend is well illustrated in Table 1[3].

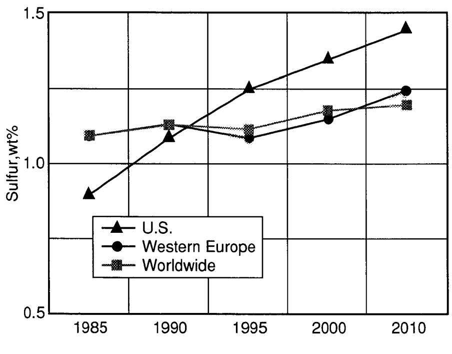


Fig.3 Typical sulfur levels in crude oil
Source: DOE EIA Petroleum supply annual, vector associates, PIRA

		Sulfur levels, wt ppm	
		Current	Target
1993	U.S.on-highway diesel	2,500	500
1996	U.S.-CARB gasoline	300	40
Europe-motor diesel		3,000	500
	Asia-motor diesel	2,000	500
1997	Asia-boiler fuel	5,000	500
1998	U.S.-CAAA complex model gasolin	400	300-350
1999	Europe-heating diesel	3,500	1,000
	Europe-bunker oil	33,000	10,000
2000	U.S.-CAAA phase II gasoline	400	50-100

Table 1 Environmental reguration on sulfuur

In all cases, the sulfur levels are being reduced into the lower ppm range. This is, again, a range where EDXRF instrumemts can perform very adequately. This cost effective technique can be directly applied to both the raw material and the finished products. This eliminates the need for multiple instruments to perform the analysis. In the very competitive petrochemical industry,this represents a major cost savings.

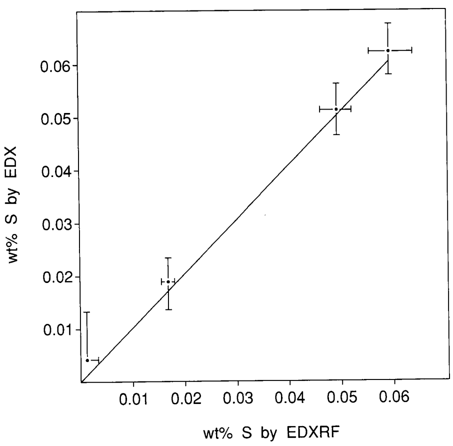


Fig.4 Means and three-sigma error bands for EDXRF (HORIBA SLFA-188/1100) and WDXFR instruments on ow sulfer diesel fuel measurements in Caleb Brett Study

As attempts are made to use EDXRF instruments for applications that have traditionally been for WDXRF, a critical issue will be the equivalency of the two types of technology. In the case of the sulfur in diesel regulation, this was actually mandated. Initial attempts at this were performed by groups of users of the technology. Examples of this type of study are work performed by Marathon Oil and a joint study by Mobil-Sun-Caleb Brett. In this work the two technologies were compared and found to produce essentially equivalent results. An example of these results are shown as Fig.4[4]. This type of data validated the expectation that the two techniques are capable of producing equivalent results.

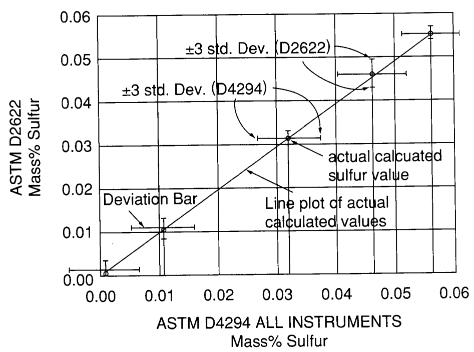


Fig.5 Method comparison ASTM D2622 vs ASTM D4294 (Modified)

In order to generalize these conclusions, an exhaustive study was performed under the auspices of the Alberta Research Council. This study incorporated data from both types of equipment at a variety of customer locations. This data is represented as Fig.5[5]. Again the conclusion was the same. At least for this application there is more than adequate proof of equivalency. As Table 1 indicates, the levels of sulfur in petroleum products is expected to continue dropping in the near future. The foregoing studies proved equivalency at 500 ppm, but that is a far cry from 40 ppm, which is anticipated. This lower level will surely require the development of new EDXRF instrumentation. These sorts of requirements have driven the evolution of new technology in the past and will again be operative. Horiba is preparing now to supply the new products in the market. This implies an instrument capable of measureing samples at 1/10 of the concentration set forth in the regulation. This new equipment will undoubtedly be evaluated exhaustively prior to acceptance. This should lead to a whole new next generation of EDXRF products.

[Reference]

1) B.Yokhin and R.C.Tisdale, "High-sensitivity Energy-dispersive XRF Technology", in American Laboratory, July 1993, p.24C-24H.
2) B.J.Price, "X-ray Fluorescence Acids QA/QC", in PI Quality, Second Quarter 1991, p.18-21.
3) D.J.Monticello, "Biocatalytic Desulfurization", in Hydrocarbon Processing, February 1994, p.39-45.
4) T.E.Stauffer, "1993 Diesel Specification Equivalency Statement", Horiba publication dated August 1993, p.4.
5) R.W.Wasel, "Determination of Low Level Sulfur Concentration in Diesel Fuel Round. Robin (S-120)", Alberta Research Council report dated December 6, 1993, p.45.

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米国市場における蛍光X線を使った元素分析の動向

エネルギー分散形蛍光X線分光分析法(EDXRF)は手軽な汎用元素分析装置として開発され発展してきた.

EDXRFは, 周囲の元素組成の影響(マトリックス効果)や軽元素の検出感度などの課題はあるが, だれもが容易に操作でき, コスト・パーフォーマンスが高いなどの特長を生かして, 変圧器用油中の塩素の分析や廃油中の磨耗金属の測定など, 各種産業のルーチン分析用として幅広く使われている.

近年の環境問題の高まりを受け, 米国では1990 Clean Air Actに対応して, EPAがディーゼル燃料中の硫黄を500ppmまでに減少させようとするなど, 各種石油製品中の硫黄含有量の規制はますます厳しくなりつつある. EPAでは, 波長分散形蛍光X線分光分析法(WDXRF)を公的な硫黄分析法(ASTM D2622)とすると同時に, ある条件下では, EDXRFを代替分析法(ASTM D4294)として認めている. 現在ホリバでは, 規制濃度の1/10を測定できるEDXRF装置の開発を進めており, 次世代のEDXRFとして牽引力となるものと期待している.
