ADVANCE IN DETECTION OF LOW SULFUR CONTENT BY WAVELENGTH DISPERSIVE XRF

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ABSTRACT

A compact wavelength dispersive x-ray fluorescence analyzer using monochromatic excitation has been developed for low sulfur content detection. In this system, two point-to-point focusing doubly-curved crystal optics were used. The first one provides monochromatic primary beam for excitation and the second one collects the sulfur(S) characteristic x-rays from a sample. Signal-to-background ratio was improved significantly due to the monochromatic excitation. Because of the large collection solid angle of double crystal optics, high sensitivity has been obtained even with the use of low power x-ray tube. Detection limits of sub ppm for sulfur in diesel was achieved using a 45W x-ray tube for 100 seconds(s) measurement time. In this paper, the basic geometry of the system and measurement data are presented and discussed.

INTRODUCTION

There is a need for a reliable and robust method for the detection of low-level sulfur in fuel due to recent EPA regulations. X-ray fluorescence (XRF) analysis has been demonstrated to be a reliable and accurate method for S detection in petroleum products. However, conventional XRF using energy dispersive spectrometry (EDS) without x-ray optics has limitation for detecting low level S in oil due to its relatively poor signal-to-background ratio (S/B). Another serious issue for any XRF/EDS system~~s~~ is that the strong scattering of the primary beam from the sample can enter and swamp the energy dispersive detector. This limits the intensity of the primary beam due to the counting limitation of the energy detector. Therefore, for high sensitivity and trace analysis, wavelength dispersive spectrometer is necessary. XRF with polychromatic excitation using wavelength dispersive spectrometry (WDS) provides better S/B, but a high power x-ray tube is necessary due to the low efficiency of WDS system. Round robin testing showed unsatisfactory results for measurement of sulfur in oil with concentration below 30ppm.

XRF analysis using monochromatic excitation can provide much better S/B than polychromatic excitation by eliminating the scattering of bremsstrahlung (continue x-rays) from the x-ray tube. Laboratory monochromatic XRF method has been hindered by the lack of efficient x-ray focusing monochromators until recently[1-4]. With innovative point-to-point focusing doubly-curved crystal (DCC) optic devices, intense monochromatic focused beams were achieved using low power compact x-ray sources. This allows a practical small spot monochromatic XRF analysis using a compact x-ray source. Due to the small beam size, a second point-to-point focusing DCC can also be used as a fixed WDS channel for collecting characteristic x-ray photons from the element of interest.

In this paper, a compact XRF/WDS system using monochromatic excitation and a fixed channel for sulfur detection will be described. Experimental data for sulfur measurement in diesel is presented and the detection limits are determined.

SYSTEM PRINCIPLE

Doubly curved crystals are the key components for this instrument. The basic geometry of a point-to-point focusing DCC was described elsewhere[3,4]. The shape of a doubly curved crystal surface is typically toroidal, and the reflection planes of the crystal are parallel to the surface. The crystal selects a narrow energy band of x-rays to satisfy the Bragg diffraction condition from a small x-ray source and focuses them to a spot. The reflection and focusing properties of DCC have been investigated both experimentally and theoretically[1,2,4].

The basic configuration of a compact XRF/WDS unit with single channel based on DCCs is shown in Figure. 1. It consists of an x-ray tube, a point-focusing DCC for excitation, a sample mount, a focusing DCC for collection and an x-ray detector. The x-ray tube has power of 10 to 50 W and its spot size is in the range of several hundreds of microns. In this system, the first-point focusing DCC captures a narrow bandwidth of x-rays from the source, typically a characteristic line of the x-ray tube, and focuses an intense monochromatic beam in a small spot on a sample. The monochromatic primary beam excites elements of interest in the sample and secondary characteristic fluorescence x-rays are emitted from the excitation volume. The second DCC, the collection crystal, collects characteristic x-rays for an element and focuses them to the detector. The collection DCC has an energy resolution of 5 to 20 eV and it only detects one element in the sample. For multiple element detection, multiple collection DCCs need to be used. The x-ray detector can be a proportional counter or a solid-state detector.

This XRF/WDS analyzer provides several advantages. The first one is that the signal/background is improved due to monochromatic excitation by the characteristic line from the source. The primary beam is highly monochromatic, and the bremsstrahlung photons with energies under fluorescence peaks can only reach the detector through scattering, therefore improving the S/B ratio drastically compared to polychromatic excitation. There are certain high-energy photons from the bremsstrahlung due to high order reflection of the DCC but their intensity is typically three orders weaker than the characteristic line intensity. The second advantage is that the focusing ability of the collection crystal also allows the use of a small-area x-ray counter for low detector noise and reliability. The third advantage is that there are no moving parts in the system. This is important for robustness and reliability. Finally, monochromatic excitation also provides another important advantage over polychromatic excitation: simplified quantification and matrix effect correction. With a single wavelength for the primary beam, the fluorescence intensity of an element in a sample can be related to its concentration by a very simple equation using fundamental parameters. This eliminates the need~~s~~ for a sophisticated software package and makes the measurement results accurate and reliable.

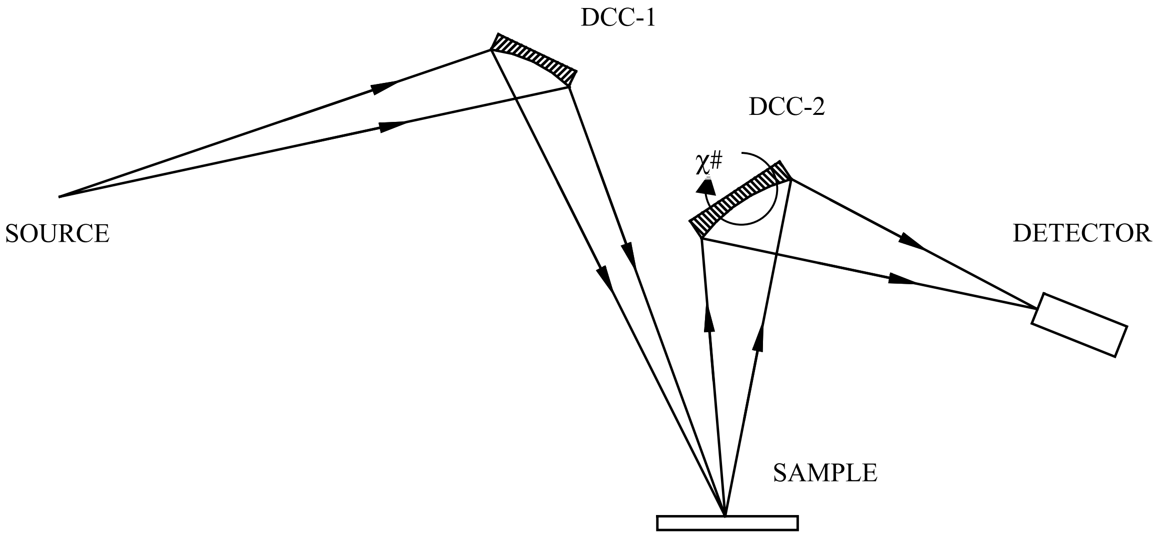

FIG. 1- THE BASIC GEOMETRY OF THE FIXED CHANNEL XRF/WDS SYSTEM WITH MONOCHROMATIC EXCITATION.

For the detection of sulfur, the energy of the excitation beam can be 2.7keV (Rh Lζ0, 3.0keV (Ag Lζ0, Sc 4.1keV (Kζ0or 5.4keV (Cr Kζ0. The analyzing crystal for sulfur can be germanium, Pentaerythritol, or quartz.

EXPERIMENTAL

Compact x-ray tubes with Ag and Cr anodes were used. Doubly curved crystal optics were designed and fabricated for focusing Ag $L\zeta_1$ and Cr Kζ1. The DCCs were characterized in air using the corresponding tube. A DCC for focusing S Kζ photons was designed and fabricated for collecting the sulfur signal from a sample. A Peltier-cooled detector with a multi-channel analyzer was used to detect the reflected x-rays from the collection DCC.

Due to the strong absorption of both the excitation beam and the fluorescence sulfur x-rays in air, a vacuum chamber was used to contain the excitation beam path and the fluorescent beam path. The chamber was pumped to 10^{-2} torr. Both the excitation DCC and the collection DCC were mounted on motorized stages in the chamber for alignment purpose. All the stages were controlled by a motion controller via a computer (PC). The PC also has a program to interface with the multi-channel analyzer for data collection.

First, the excitation beam was optimized by the alignment of the DCC to the x-ray source. The intensity of the excitation beam was measured by the detector with an attenuator to avoid the detector saturation. The focal spot size of the excitation beam was measured using the knife-edge scan method. With the excitation beam optimized, a pure sulfur powder was pressed on a flat surface and it was mounted on the sample stage for the collection crystal alignment. The energy resolution of the collection crystal was determined by the χ scan of the collection DCC. The focal spot of the collection crystal at the detector was also measured using the knife-edge scan method.

A set of diesel samples with known low S concentration was obtained from Accustandard. They include the sulfur concentration of < 200ppb, 5ppm, 10ppm, 15ppm, 20ppm, 100ppm, and 200ppm. These samples were mounted into the system and the data were collected for 100s and 900s.

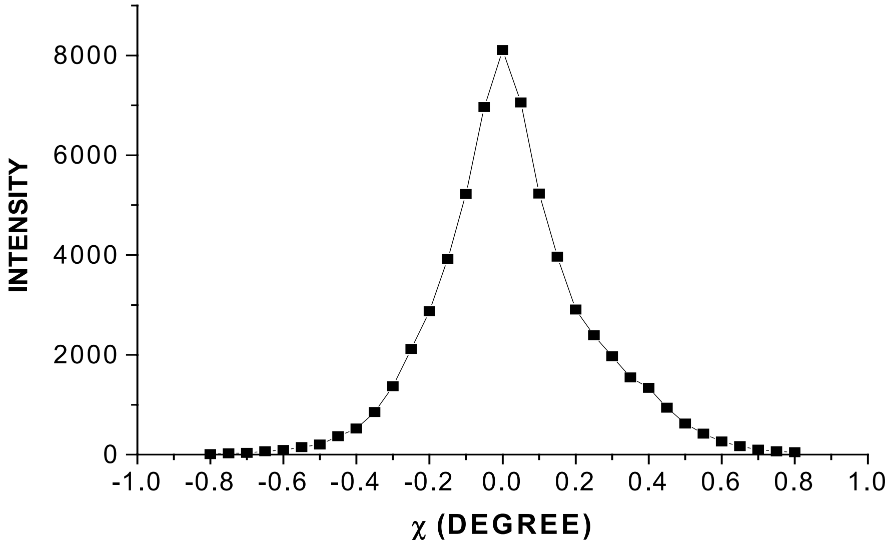

FIG. 2- THE χ SCAN CURVE OF THE COLLECTION DCC.

RESULTS

FOCUSING AND REFLECTION PROPERTIES OF THE DCC

The focusing energy, collection solid-angle, and focal distance of the excitation DCC are listed in Table I. The measured intensity and focal spot size of the excitation beam is also given. The x-ray tube is a Cr anode with maximum power setting of 50kV and 1mA. The value of the beam intensity was obtained with the source setting of 45kV and 1mA. Similarly, the characteristics of the collection crystal are given in Table II. The energy resolution of the collection crystal is determined by its rocking curve scan. The rocking curve scan (χ scan in Figure.1.) with a pure sulfur sample is shown in Figure.2. The angular width (FWHM) of the χ scan was found to be 0.35^{o}. The corresponding energy resolution is 10eV.

As shown in the Tables, both excitation and collection crystals had large collection solid angle. The excitation beam intensity was very strong even with a 45W x-ray tube.

TABLE I- MEASURED PROPERTIES OF THE EXCITATION DCC

FOCUSING ENERGY	FOCAL DISTANCE	BEAM INTENSITY	FOCAL SPOT	SOLID ANGLE
5.4 keV	120 mm	5.4 x 10^9 photons/s	200σm	0.025 sr.

TABLE II- MEASURED PROPERTIES OF THE COLLECTION DCC

FOCUSING ENERGY	FOCAL DISTANCE	ENERGY RESOLUTION	BEAM SIZE	SOLID ANGLE
2.3 keV	108 mm	9.8eV	500σm	0.1 sr.

MEASUREMENTS OF LOW SULFUR DIESEL SAMPLES

With the system at optimum alignment condition, fluorescence data were collected for low sulfur diesel standards. An energy window was selected to integrate the total counts of the S peak for each measurement for 100s. For each data point, the measurement time is 100s and the source setting is at 45kV and 1mA. The background measurement was done by using a blank diesel standard that had sulfur concentration below 200ppb. For each sample, multiple measurements were taken and the measurement results are shown in TABLE III. The total mean count was plotted vs. the S concentration in diesel samples and it yields very good linearity as shown in Figure. 3. The standard deviations ω were determined based on the multiple measurements and they were converted to the corresponding concentration based on the linear fitting of Figure. 3. The measured ω was compared with the standard deviation based on the counting statistics and is shown in TABLE III. The measured ω are very close to that of the counting statistic, indicating good repeatability of the system.

TABLE III- DATA FOR 100S MEASUREMENT TIME

STANDARD SAMPLES	# OF MEAS.	MEAN TOTAL	ω########## #PPM)	MEASURED PRECISION	STATISTICAL PRECISION
200ppm	7	3376	6.7	3.3%	1.7
100ppm	5	1627	1.5	1.5%	2.5
20ppm	24	369	1.3	6.5%	5.6
15ppm	70	301	1.0	6.3%	6.4
10ppm	17	207	0.90	8.4%	8.0
5ppm	9	123	0.66	11.7%	12
Blank	9	29	0.31	--	--

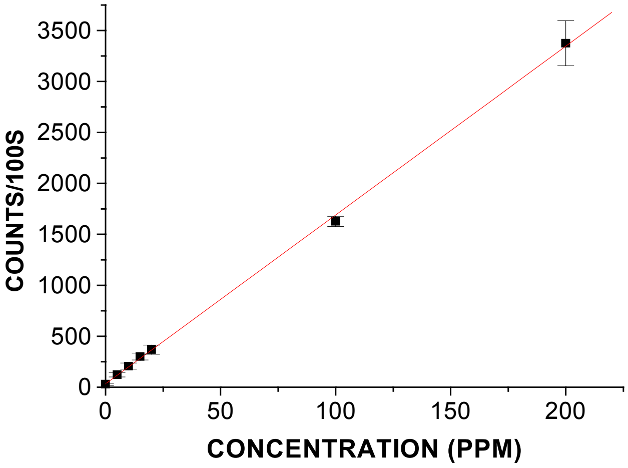

FIG. 3- THE LINEAR RELATIONSHIP BETWEEN TOTAL COUNTS AND THE SULFUR CONCENTRATION(100 second count time)

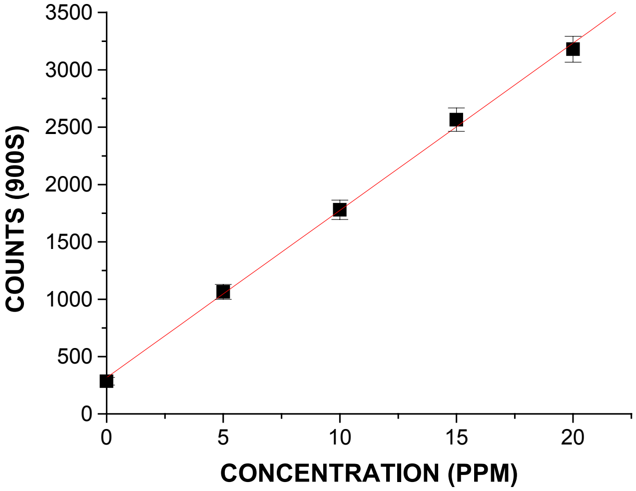

FIG. 4- TOTAL COUNTS VS. CONCENTRATION FOR 900S MEASUREMENT TIME (900 second count time)

To obtain relatively good precision, the fluorescence data for the blank, 5ppm, 10ppm, 15ppm and 20ppm samples were collected for 900s and the results are shown in Figure. 4 and TABLE IV. Only one measurement for each sample was taken and the ω and precision was estimated by the counting statistics.

TABLE IV- DATA FOR 900S MEASUREMENT TIME

STANDARD SAMPLES	TOTAL COUNTS.	ω######## #PPM)	STATISTICAL PRECISION
20ppm	3180	0.37	1.9%
15ppm	2566	0.34	2.2%
10ppm	1780	0.28	2.8%
5ppm	1064	0.22	4.1%
Blank	285	0.11	---

MINIMUM DETECTION LIMITS

Minimum detection limits (MDL) can be determined based on three times the standard deviation of the background (in concentration based on the calibration curve). Assuming the background level is the same as the result of the blank sample, for 100s measurement time, the MDL is given by MDL(100s) = 3 x 0.31 ppm=0.9 ppm based on the measured ω of the blank sample. For 900s, the MDL is estimated to be MDL (900s) = 0.3 ppm based on the counting statistics.

The limits of quantification (LOQ) is given by 10 times the standard deviation of the background. For 100s measurement time, the LOQ is determined to be 3ppm. For 900s measurement time, LOQ is 1ppm based on the counting statistics.

DISCUSSION

Excellent detection limits for sulfur in diesel are demonstrated using a compact XRF/WDS system with monochromatic excitation. This is due to the improvement of the S/B ratio using monochromatic excitation compared to conventional XRF/WDS system. For a state-of-the-art conventional WDS system[5], which uses a high-power sealed tube (2 kW), the S/B ratio for a 10ppm S diesel sample is 0.5. For this XRF/WDS system using a 45W compact tube with doubly curved crystals, the S/B ratio for a diesel sample with 10ppm S content is 6:1 based on the data in TABLE III. This is more than 10 times better than the conventional high power system.

More importantly, the system described in this paper has great potential for on-line sulfur measurement for petroleum industry due to its unique features. The x-ray tube used in the system is very low power and no liquid cooling is required. Minimum maintenance will be required for the tube. The system is designed to be robust because no moving parts are used. The very small beam size of several hundred microns, compared to 10-20 mm beam for a conventional system, allows the use of a small x-ray window in an on-line sampling system to ensure reliability.

Even better results will be expected in the future because the configuration of the source-DCC for the excitation beam is not optimized. The x-ray tube used in the experiment had limited range of accessible solid angle to the excitation DCC . An improvement of 4X is possible when using a large opening field angle combined with a DCC with a larger azimuthal angle.

CONCLUSION

A compact XRF/WDS system using monochromatic excitation was developed for low-level sulfur quantification in diesel. Two doubly-curved crystal optics were used in the system. One provided an intense monochromatic beam for excitation and the other collected sulfur fluorescence x-rays from the sample. The capability for quantification of sulfur level at low ppm range was demonstrated by measuring a set of diesel standards with low sulfur content. Detection limits of 0.3ppm and 0.9ppm were achieved for 900s and 100s measurement time respectively. Quantification limits of 1ppm and 3ppm were shown for 900s and 100s measurement time respectively. A precision of 8% was obtained for a diesel with 10ppm sulfur content within 100s and a 3% precision was achieved if 900s measurement time was used. This system has great potential for an on-line application for sulfur content determination in the petroleum industry.

REFERENCE

1. Wittry, D. B. and Sun, S. “X-ray Optics of Doubly Curved Diffractors,” J. Appl. Phys. Vol. 71, 1992, pp564-568.
2. Wittry, D. B. and Sun, S. “Focussing Properties of Curved Diffractors,” J. Appl. Phys. Vol. 68, 1990, pp387-391.
3. Chen, Z. W. and Wittry, D. B., “Microanalysis by monochromatic microprobe x-ray fluorescence – physical basis, properties, and future prospects”, J. Appl. Phys. Vol. 84, 1998, pp1064.
4. Chen, Z. W., “Recent development of doubly-curved crystal focusing optics and their applications for micro XRF”, SPIE, Vol. 3767, 1999, pp114.
5. Uhlig, S. and Buehler, A., “XRF for sulfur control”, Hydrocarbon Engineering Vol.5, Iss. 9, 2000, pp 54-65.