CHAPTER 4

MATERIALS AND METHODS

The purpose of this research is to design and construct a two channel XRF spectrometer for S and Pb analysis in fuel oils. The spectrometer must be cheap, portable and easy to operate. A gas filled proportional X-ray detector and radioactive sources which are available at Department of Nuclear Technology and STREC* of Chulalongkorn University are therefore used throughout this research.

Before designing and constructing the two-channel spectrometer, the sample-source-detector geometry and techniques of analysis are studied using the proportional detector and sources and commercially available pulse-height analyzers, both SCA and MCA. The two-channel spectrometer is then designed, constructed and tested electronically prior to the final test for S and Pb analyses. The procedures can be summarized as follows:

(i) determination of appropriate sample-source-detector geometry using an MCA

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*Scientific and Technological Research Equipment Centre.

(ii) Study of S and Pb X-ray measurements using an SCA

(iii)analysis of S and Pb using an SCA and compare with those obtained by the S and Pb analyzer of the Esso Standard (Thailand) Co., Ltd.

(iv) design, construction and test of the two channel analyzer.

(v) analysis of S and Pb using the two channel analyzer.

4.1 Materials

The materials which are used throughout this research are as follows:

4.1.1 MCA: composing of HV Power Supply ORTEC Model 456, Xe-filled detector, 15x5x5 cm^3, Preamplifier CANBERRA Model 2006E, Amplifier ORTEC Model 575A, MCA TRACOR NORTHERN Model TN 1706 and TN 1314, and NIM BIN ORTEC Model 4001.

4.1.2 SCA: composing of HV Power Supply ORTEC Model 456, Xe-filled detector 15x5x5 cm^3, Preamplifier CANBERRA Model 2006 E, SCA CANBERRA Model 2030, Timer ORTEC Model 773, Counter ORTEC Model 775, and NIM BIN ORTEC Model 4001.

4.1.3 The detector chamber.

4.1.4 Radioactive sources: Fe-55 ($7.4x10^8$ Bq) and Cd-109 ($7.4x10^8$ Bq) annular sources.

4.1.5 Polyethylene sample holders for liquid samples.

4.1.6. Standard elements, as S, Ar (in air), Fe, Ni, Zn, As and Pb.

4.1.7 Acrylic cylindrical tubes with inner diameter of 4.25 cm. and heights from 7 to 12 mm.

4.1.8 Oscilloscope TEKTRONIX Model 2465 A.

4.1.9 Pulser NT 1503 A.

4.1.10 Electrostatic Voltmeter Model ESD-9, 0-3000 V. ranges.

4.1.11 High octane gasoline samples

4.1.12 Diesel oil samples

4.1.13 Pb standard solution

4.1.14 S standard solution

4.1.15 The S and Pb analyzer of the Esso Standard (Thailand) Co., Ltd., Princeton -tech Model 100 and 102.

4.2 Methods

4.2.1 Determination of the Optimum Sample-Source-Detector Geometry for Sulfur Analysis with the MCA

In the measurement of S K X-rays, the K X-rays of the 0.8 % argon gas in air sometimes interfere especially when sulfur content in sample is very low. There are two possible ways to minimize the interference. Firstly, the sample-source-detector is optimize in order to minimize the amount of air between the sample and the detector. In this case the source can be placed in close contact with the detector but the sample must be placed some distance away from the source surface to obtain good excitation and detection efficiency of sulfur fluorescent X-rays. In practice the optimum distance can be determined from the ratio of sulfur X-rays intensity to the corresponding background.

Tangpoonpholvivat, K. (1986)[7] found that the optimum distance is 3 mm. for the S analysis. However, the optimum distance is detected to confirm by the MCA.

Secondly, the excitation and detection of sulfur X-rays must be done in the nitrogen or helium atmosphere.

When a Xe-filled detector is used with an Fe-55, the escape peak of Mn K X-rays will appear at the lower end of the spectrum and interfere the sulfur X-rays fluorescence. It is unavoidable and prominent when the S content is low or the sample has high scattering coefficient.

For Pb analysis, the optimum distance in the S analysis can also be used since the distance does not greatly affect the measurement of Pb L X-rays.

The experimental procedure is as follows:

- The Fe-55 annular source is placed above the detector. The cylindrical tube. 7 mm. which is used to support the sample holder is then placed over the source. The sample holder containing 10 ml. of white oil which is used as the blank solution for the S analysis is then placed above the tube.

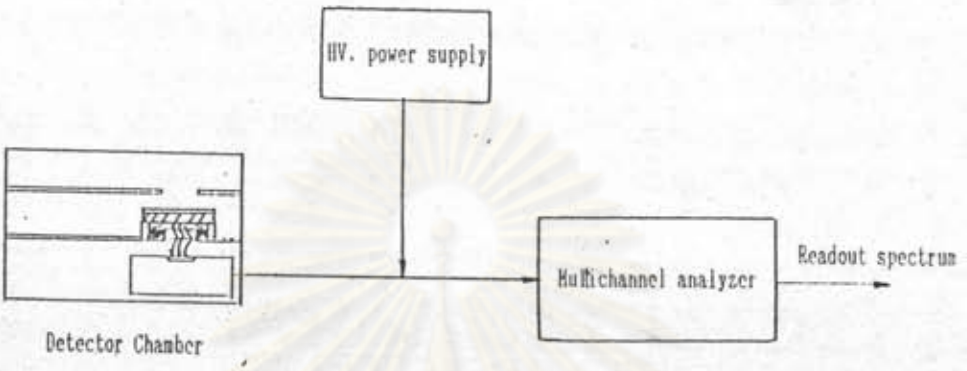

Fig. 4.1 Block diagram of X-ray fluorescence analysis using MCA.

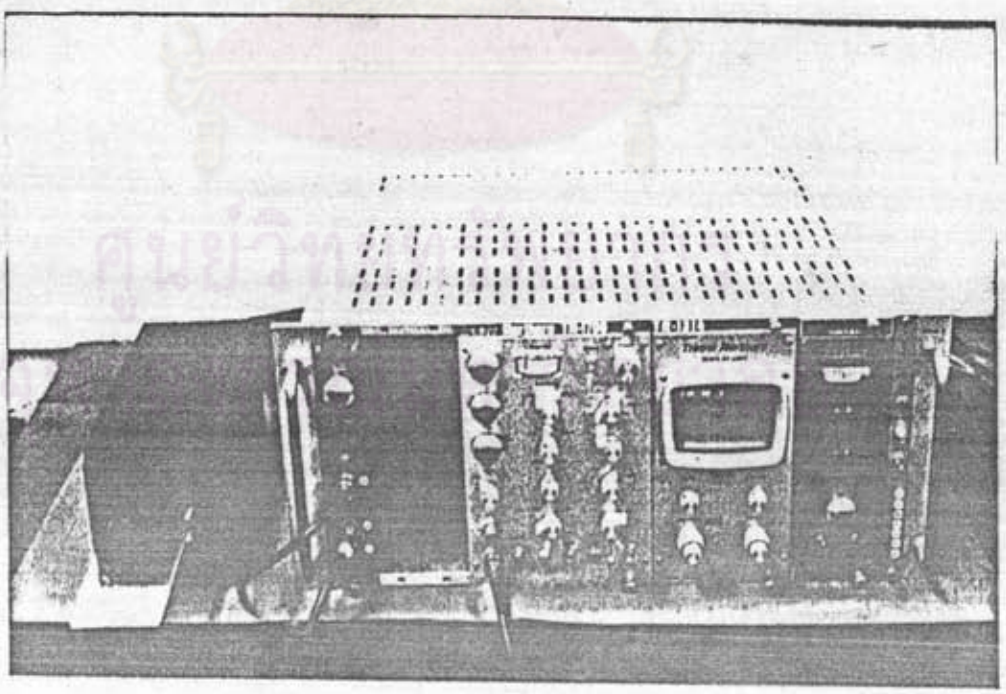

Fig. 4.2 Photograph showing XRF analysis using MCA.

- Adjust the amplifier gain to get the favourable spectrum and then measure the spectrum for 300 seconds. The appropriate amplifier gain for a set of MCA and SCA in this research is coarse gain = 40 and fine gain = 12.

- With the same settings, repeat the above steps with the cylindrical tubes 8, 9, 10, 11 and 12 mm.

- Determine the optimum source-to-sample distance.

4.2.2 Energy Calibration of the SCA

With the same geometric arrangement as in 4.2.1, The energy calibration for S and Pb analysis using the SCA is obtained from the following standards: S, Ar (in air), Fe, Ni, Zn, As and Pb. For determining the S and Ar peaks, Fe-55 is used while Cd-109 is used for the rest. The experimental procedure is as follows:

- Find the peak position of the above standard elements using window (ΔE) setting 0.05 volt and the LLD increment 0.05 volt.

- Plot the energy calibration curve and determine the appropriate LLD and ΔE setting for S and Pb analysis.

4.2.3 Sulphur and Lead Analysis with the SCA

S K fluorescent X-rays are detected from 0.60 through 0.80 volt (LLD = 0.6 volt, ΔE= 0.2 volt) which is equivalent to 1.978 keV - 2.638 keV energy range and Pb L fluorescent X-rays

are detected from 3.50 through 5.55 volt (LLD = 3.50 volt, ΔE = 2.05 volts) which is equivalent to 9.748 keV - 15.458 keV energy range. The results are compared with those obtained the commercial S and Pb analyzer of the Esso Standard (Thailand) Co., Ltd. The experimental procedure is as follows:

- Measure the standard sulfur solutions with contents of 1.05 %, 0.75 %, 0.50 % weight and the blank solution for 300 seconds.

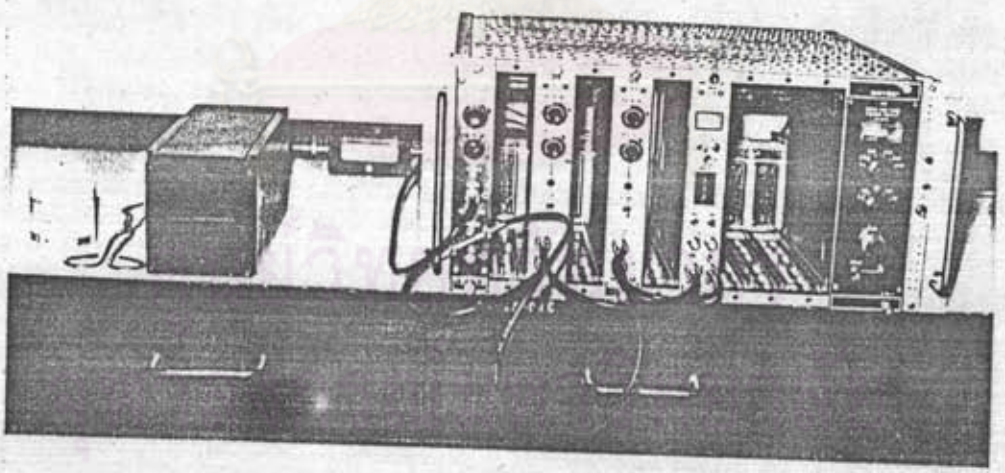

Fig. 4.3 Picture of the SCA and the detector chamber.

- Plot the count rates against the S contents.
- Count the diesel oil samples for 300 sec. each and determine the S contents using the content calibration curve.

- Repeat the above steps with the Pb standards with contents of 0.415, 0.30, 0.25, 0.15, 0.0 gm/l, and the high octane gasoline samples.

- Analyse all samples using the commercial S and Pb analyzer then compare the results.

4.2.4 Two Channel Analyzer

After the comparison of SCA with the commercial S and Pb analyzer their efficiency is close significantly. Therefore, two channel analyzer is designed, constructed and tested in the following conditions:

(a) the high voltage power supply, providing the operating bias for detector, in range of 0-2500 volts,

(b) the amplifier with a gain in range of 100-500 times,

(c) two set of single channel analyzer, one for S analysis, the other for Pb analysis,

(d) counter and timer,

(e) the low voltage power supply, providing $\pm$24, $\pm$12, +9 and +5 regulated voltage.

High Voltage Power Supply

By using the principle of HV. power supply in the previous chapter, DC to DC converter and Voltage regulater are constructed. The high voltage power supply unit is required to test the linearity and ripple of output voltage. By using the

setup from Fig. 4.5, the linearity of HV. is determined by varying the dial and recorded the voltage output from electrostatic meter. The result of linearity is shown in Table 5.6 and Fig. 5.6. The ripple voltage of HV. output at 2500 volts, reading from an oscilloscope shows that the ripple voltage is less than 200 mV.

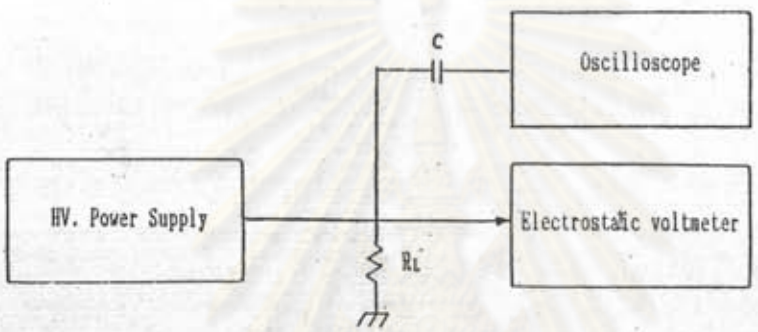

Fig. 4.4 Block diagram of the high voltage testing.

Amplifier

The amplifier comprises of the charge sensitive preamplifier, the adjustable gain and pulse shaping amplifier. It is constructed and tested in the amplifier gain and pulse shape.

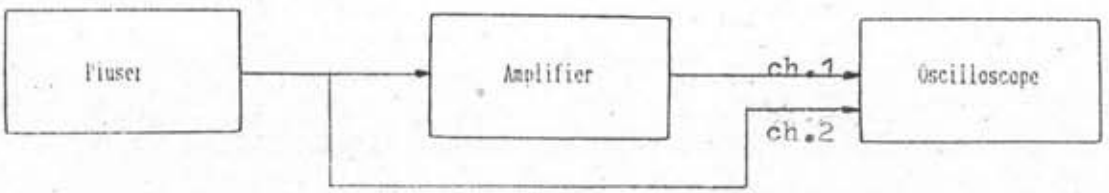

Fig. 4.5 Block diagram of the amplifier gain testing.

Connect the equipment as shown in Fig. 4.6. The amplifier gain and the pulse shaping are obtained by varying the pulse height of pulser (Ei) in steps and each time record the peak height, reading on oscilloscope. The result is shown in Table 5.7 and Fig. 5.7.

Single Channal Analyzer

The main point of single channel analyzer (SCA) is the linearity of voltage level discriminator, so it is necessary to test the linearity after SCA is constructed.

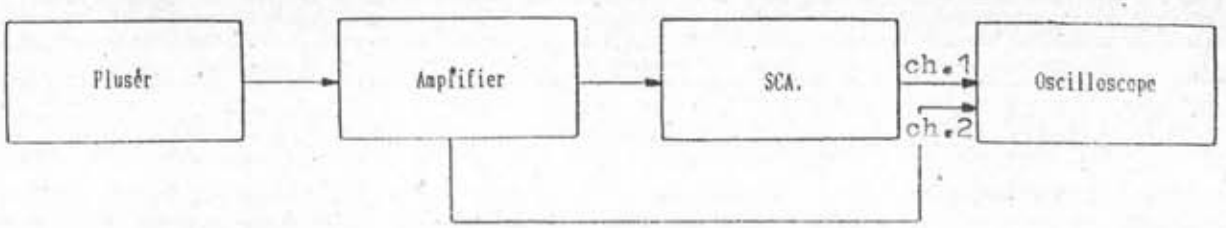

Fig. 4.6 Block diagram of the linearity test of the SCA.

Setup the equipment as shown in Fig. 4.6, the linearity of LLD and ULD for each channel can be tested with a pulser as follows:

- With the attenuation switch to x10 and x10 and pulse height control at 10, adjust the amplifier gain until obtain output pulse of 10 V. amplitude on the ch. 1 of oscilloscope
- Keeping the ULD control fix at 10.0, check the linearity of LLD control by varying of PH. control in steps. Record the readings of LLD scale while varying PH. for each half triggering (HT) is obtained.
- Keeping the LLD control fix at 0.0, check the linearity of ULD control by varying of PH. control in steps. Record the readings of ULD scale while varying PH. for each HT. is obtained.

The testing results of LLD and ULD for two channel analyzer are shown in Table 5.8 and Fig. 5.8.

Scaler and Timer

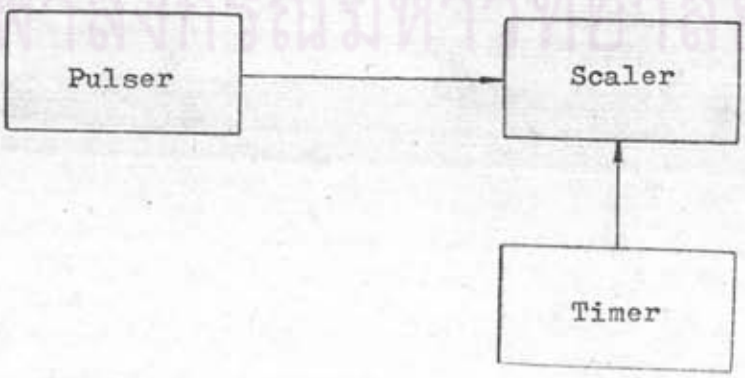

Fig. 4.7 Block diagram of the scaler and timer testing.

Connect the system as shown in Fig. 4.7. Keeping a pulse height control of the pulser constant at 2 volts. Increase the set time, 1, 10 and 100 sec. In each of the set times, the scaler is displayed the count of 50, 500 and 5000, respectively.

4.2.5 Sulfur and Lead Analysis by Two Channel Analyzer

According to the S and Pb analysis by an SCA the appropriate conditions, amplified gain, operating voltage for detector, the ranges of S and Pb X-ray spectra and sample-source-detector geometry, are set in two channel analyzer.