# Model SLFA-1800 Fluorescent X-ray Analyzer for Sulfer in Oil

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Abstract

For approximately the past twenty years, anti-air-pollution activities have made use of fluorescent X-ray analyzers that enable the simple measurement of sulfur concentration in fuel oil and heavy oil. In recent years, as environmental problems have become increasingly acute, the technology of sulfur analyzers has become progressively sophisticated. Horiba's Model SLFA-1800, an easy-to-use sulfur analyzer introduced in August of 1991, offers numerous new features, including correction for temperature and atmospheric pressure, automatic gain control, and self-diagnosis functions. As a result, the SLFA-1800 is much easier to use and simpler to maintain; in addition it is much more resistant to changes in temperature and atmospheric pressure. This has improved the long-run reliability and eliminated warm-up time.
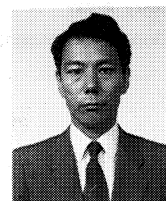
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1. Introduction

The first model of Horiba's SLFA Series was the SLFA-200; introduced in September of 1974, this was the first Japanese sulfur analyzer to use an X-ray tube. The SLFA-200 contained a primitive LSI chip capable of handling addition, subtraction, multiplication, and division; this made it an advanced piece of equipment for its time. Following this, Horiba marketed the SLFA-300 and the SLFA-500.
These were superseded by the SLFA-800 and the SLFA-920. A model change resulted in the introduction of the new SLFA-1800 in August of 1991. Thus far, Horiba has shipped more than 1,000 units of the SLFA Series.
SLFA Series models are being used throughout the world, primarily in Japan, North America, South America, Southeast Asia, the Middle East, and across Europe.
SLFA analyzers are used mainly to measure sulfur concentration in petroleum-based fuels. When the sulfur compounds in fuel oils are burned, they become sulfurous acid gas. Sulfurous acid gas is not only a major cause of air pollution, it is one of the elements underlying acid rain, which has become a serious environmental problem in recent years. Thus the measurement of sulfur concentration has become increasingly more important. In addition, public awareness of global environmental problems has heightened; this can be expected to result in even more stringent controls on emission pollutants, leading to demands for greater precision in the measurement of sulfur concentration.
This paper will first look at the principles of measurement used in the SLFA Series. Then it will consider the features and major functions of the model SLFA-1800 analyzer.
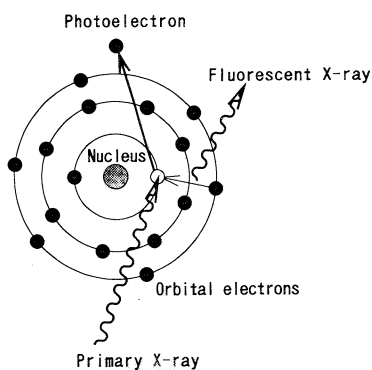
2. Principles of measurement
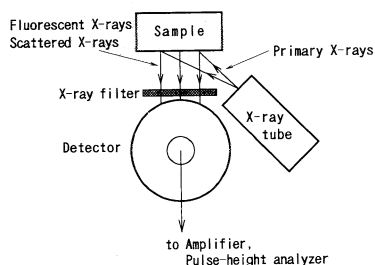

Fig.1 Generation of fluorescent X-rays

Fig.2 SLFA-1800:Principles of measurement

* eV, or *electron volts*, is commonly used as the unit of energy in X-rays. 1 eV is equivalent to 1.602×10^{-19} joules. If the energy E is expressed in thousands of eV, or keV, and the wavelength of the X-rays λ is expressed in Angstroms $\mathring{A}(0.1nm)$, then $\lambda = 12.4/E$.

Several methods are available for the testing of sulfur concentration in petroleum products. These are specified by such guidelines as those of the American Society of Testing Materials (ASTM) and the Japanese Industrial Standards (JIS). The SLFA Series are energy-dispersive, radiation-type analyzers that use X-rays. As such they fall under the following guidelines: ASTM D4294-90, ISO/DIS 8754, JIS K2541-1984, and JIS K7995-1984.

X-rays, as used in the SLFA Series, are high-energy electromagnetic waves of extremely short wavelength. When these X-rays are focused on an atom, the photoelectric effect results in ionization, and a vacancy is created by the missing core electron. When an outer electron moves to fill that vacancy, the binding energy difference causes the emission of an X-ray of a corresponding energy. (See Fig. 1.)

The X-rays thus emitted will have an energy level characteristic of the atoms of element they emanate from. These are referred to as characteristic X-rays. If these characteristic X-rays have been generated by excitation of the atoms by other X-rays (i.e., *primary X-rays*), they are also called *fluorescent X-rays*.

The SLFA Series use fluorescent X-rays in the analysis of sulfur. As Fig. 2 shows, primary X-rays, generated by an X-ray tube, are focused on the sample material. A portion of the primary X-rays will excite the atoms of the sample material, resulting in the generation of fluorescent X-rays. Most of the remaining primary X-rays will be scattered by the sample material. These scattered X-rays will have an energy approximately the same as that of the primary X-rays; the SLFA Series uses titanium as the target material of the X-ray tube to generate its primary X-rays, most of which have an energy of 4.5 keV* If we assume that the primary X-rays always have the same strength, then the amount of fluorescent X-rays of sulfur generated will be approximately proportional to the amount of the sulfur in the sample (fluorescent X-rays of sulfur have an energy of 2.3 keV).

Both the fluorescent X-rays and the scattered X-rays emanating from the sample enter a proportional-counter type detector and are transformed into electric signals. These signals are boosted by an amplifier and then passed through a multi-channel pulse-height analyzer to obtain the energy spectrum.
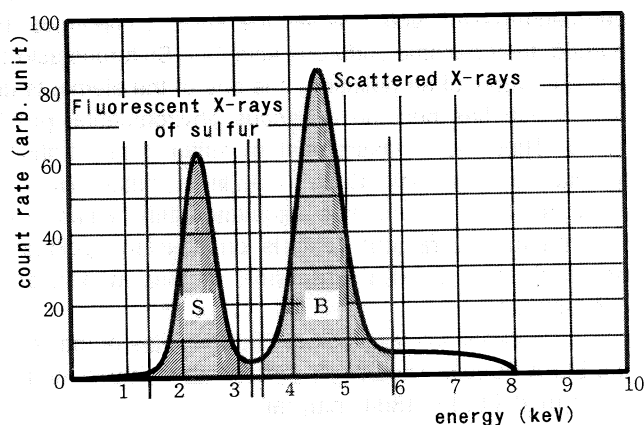

Fig.3 Energy spectrum of sulfur measured by the fluorescent X-ray analyzer

Fig. 3 shows the energy spectrum of the fluorescent X-rays of sulfur and the scattered X-rays as measured by a proportional counter. From this spectrum, we can obtain the sulfur concentration from the two shaded areas: S, the area corresponding to the fluorescent X-rays of sulfur, and B, the area corresponding to the scattered X-rays. Specifically, a calibration curve is first derived from standard samples that have known sulfur concentrations. This calibration curve is then used to calculate the sulfur concentration of the sample in question.

However, in measuring the actual spectrum, it becomes clear that there are several problems. One is shown in Fig. 4A. To the right of the peak of the fluorescent X-rays of sulfur, it can be seen that fluorescent X-rays of argon are also measured by the detector. Atmospheric air contains approximately 1% of argon by volume; the primary X-rays hitting this argon generate fluorescent X-rays of argon, at an energy level of approximately of 3.0 keV, overlapping with the peak of fluorescent X-rays of sulfur.

To prevent this interference from argon, the SLFA Series use a niobium membrane as an X-ray filter in front of the incident window on the detector. The filter blocks the fluorescent X-rays of argon. Niobium has an absorption edge at 2.4 keV; once this energy level is exceeded, the absorption coefficient rapidly increases. Therefore, the fluorescent X-rays of argon are absorbed and do not pass the filter; but there is little absorption of the fluorescent X-rays of sulfur, which are allowed to pass.

Fig 4B shows the spectrum obtained with this filter. There is no effect from the argon, and the fluorescent X-rays of sulfur show a single, easily distinguished peak at the left.
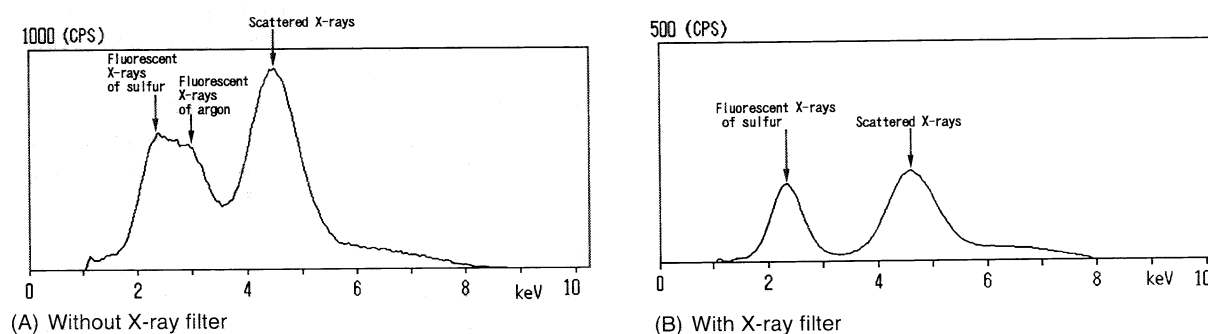

(A) Without X-ray filter   (B) With X-ray filter

Fig.4 Energy spectrum measured by the SLFA-1800

A second problem is that X-rays are absorbed by the air. In general, X-rays are powerful enough to be able to pass through most physical substances. But with the X-rays of the energy level used in the SLFA Series, we cannot discount X-ray absorption by the air. For example, for the characteristic X-rays of sulfur, approximately 30% will be absorbed by a 10-mm layer of air at 20flC and one atmosphere of pressure.

The rate of absorption into the air varies not only with the thickness of the layer of air the X-rays pass through; it also varies with the density of the air itself, i.e., with temperature and atmospheric pressure, which cannot be maintained constant for each measurement. Therefore, to assure measurement accuracy, it is necessary to measure the air temperature and pressure and to correct for the amount of X-ray absorption.

The SLFA-1800 checks the air temperature and pressure at each measurement and makes a correction for the amount of X-ray absorption. The graphs in Figs. 5 and 6 show the effect of temperature and atmospheric pressure. As can be seen, this is greatly reduced after correction by the SLFA-1800.
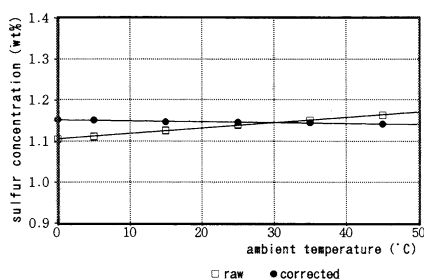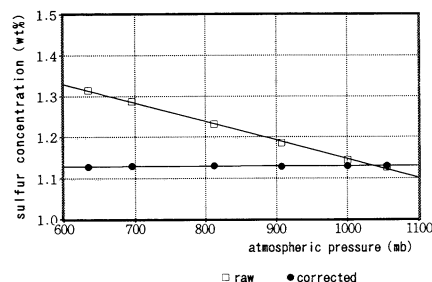

Fig.5 SLFA-1800 results after temperature correction

Fig.6 SLFA-1800 results after correction for atmospheric pressure

3. An overview of the analyzer

3.1 Configuration of the SLFA-1800

The SLFA-1800 was developed with the basic concept that it should be user-friendly. Therefore, all readouts are displayed on a large, easy-to-read, backlit liquid crystal monitor. The number of keystrokes has been reduced to a minimum. Measurement can be performed just by the push of one key.

The control panel has been greatly simplified. There are only 21 keys in all: the switch to start measuring, four function keys, and a 16-key central keypad. Calibrations, which need to be performed regularly, are simple to perform just by using the four function keys in response to on-screen instructions from the CPU.

Fig. 7 is an external view of the SLFA-1800. It is quite compact, only 430 mm wide, 500 mm long, and 215 mm high. Weighing only 27 kg, the SLFA-1800 is by far the lightest of any sulfur analyzer using an X-ray tube.

Fig 8. is a flow diagram showing the main functions of the SLFA-1800. Units shaded with hatched lines are additions new to the SLFA-1800. The X-ray tube is the same as that used in earlier models in the SLFA Series; it operates at 8 kV and 30 É A, and titanium is used as the target material. The proportional counter used as a detector is sealed with neon gas.

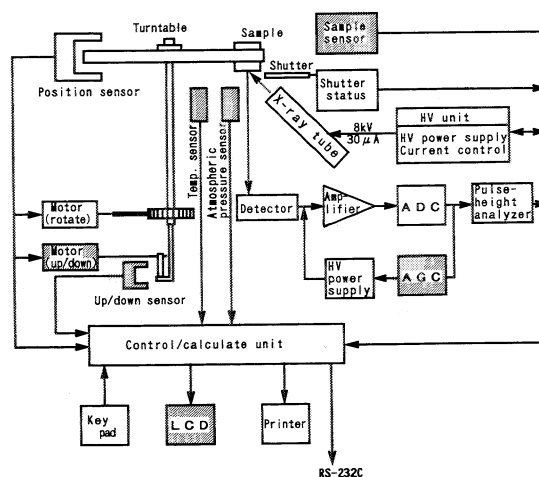Fig.7 Model SLFA-1800 fluorescent X-ray analyzer for sulfur in oil

Fig.8 Block diagram of the SLFA-1800

3.2 Features of the SLFA-1800

(1) Automatic gain Control

When the proportional counter has been used for long periods of time, the output pulse height will tend to decrease. This is the result of several factors, including changes in the composition of the internal gas in the counter tube. If this happens, the peak will shift to the left in the spectrum results, i.e., in the direction of lower energy, making it difficult to obtain correct measurements.

In addition, the gain of the amplifier and the ADC will also be affected by variations in the ambient temperature and by changes that take place over periods of extended use. These effects can also result in spectrum peak shifts. The SLFA-1800 incorporates a feature to eliminate this peak shift and to assure that stable measurements are obtained.

In general, the output from proportional counters varies greatly with changes in the applied voltage. Fig. 9 shows the relationship between the applied voltage and the output pulse height of a typical proportional counter. As can be seen here, the pulse height becomes greater as the applied voltage increases; conversely it drops as the applied voltage decreases.

Regardless of the amount of sulfur contained in the sample, the SLFA-1800 can always detect the peak of the scattered X-rays (i.e., the characteristic X-rays of titanium). The SLFA-1800 uses the position of this scattered-X-ray peak to adjust the gain. This is done by increasing or deceasing the applied voltage to the proportional counter so that this position agrees with the position of the characteristic X-rays of titanium. This feature is called the automatic gain control, or AGC.

The AGC functions constantly during SLFA-1800 measurements and it is responsive to sudden ambient changes that might affect measurements. As was mentioned above, the pulse height of the proportional counter will gradually deteriorate with age. But the SLFA-1800's AGC function automatically adjusts the applied voltage if it detects any drop in the pulse height output. This means there is no need to make manual adjustments to either the amplifier gain or the high voltage to the proportional counter.

Fig.9 Applied voltage vs. pulse-height characteristics of the proportional counter

(2) Self-diagnostic function

Both the X-ray tube and the proportional counter used in the SLFA Series are sealed tubes; thus they have a limited life and will need to be replaced over time. With the model SLFA-1800, as the time for replacement approaches, a warning message appears on the LCD screen, enabling you to replace the tube before it fails.

The proportional counter is checked by the amount of applied voltage necessary to correct for the falling output pulse height. The X-ray tube is checked by the grid voltage that controls the current to offset cathode deterioration. Separate warning messages are shown on-screen for these. If the components are replaced when indicated, continuous measurements can be made with no deterioration in the accuracy of the unit.

In addition, numerous other checks are made for possible malfunctions, including a burnt-out X-ray tube filament, possible voltage and current abnormalities, and failure of any of the various sensors located throughout the unit. If any abnormalities are detected, the self-diagnostic function shows the problem by on-screen error warnings. Details of these error warnings may also be directed to the printer. This function makes it easy to locate the source of trouble should any abnormality or malfunction arise.
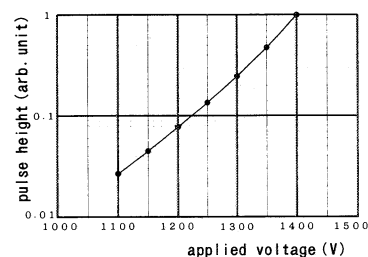
(3) Data output

It is becoming increasingly common to use PCs or microcomputers in the laboratory to collate and organize measurement data. A wide range of computer hardware and application software is generally available for data analysis.

Therefore, it was felt unnecessary to equip a compact, portable analyzer like the SLFA-1800 with its own computing power. Instead, the SLFA-1800 was designed to transmit its results via a standard RS-232C serial port to an MS-DOS PC or other computer. This has the advantage of allowing greater freedom in handling the results obtained by the SLFA-1800, and it also keeps the design and the operation of the SLFA-1800 as simple as possible.

With the SLFA-1800 connected to an external computer, it transmits data (1) when measurements are made, (2) during auto-calibration, and (3) when a spectrum is obtained. For ease of use and general application, the SLFA-1800 transmits its data in ASCII code. This allows data handling in BASIC or with any of a number of commercially available software packages.

(4) Additional features

The SLFA-1800 has several desirable new features. A turntable holding eight sample cells automatically and accurately loads each sample cell, placing the cell window in the proper position for measurements. This eliminates the need to load each different cell in position by hand. Leakage is always a problem when handling fuel oils. The SLFA-1800 is equipped with a protective membrane to protect the detector incident window from any splash or leakage from the sample cells.

For safety, all switches are backed up by a duplicate circuit. To ensure X-ray safety, the SLFA-1800 is ingeniously designed with fail-safe shielding configurations, eliminating any possibility of X-ray leakage.

4. SLFA-1800 performance

4.1 Repeatability

With analyzers like the SLFA-1800, an important performance benchmark is *repeatability*. Repeatability as used here refers to the standard deviation (or more precisely the sample standard deviation σ_{n-1}) obtained when taking repeated measurements of the same sample. This is different from the "repeatability" used by ASTM, JIS, etc. For purposes of discussion here, we will take *repeatability* to mean simply the standard deviation.

For the SLFA-1800, repeatability is determined mainly by the statistical error. This paper will give only an overview; for a detailed discussion, the reader is directed to standard references on statistics and radiation measurement.[1,2,3]

As explained above in the principles of measurement, the SLFA Series uses an X-ray count. In radiation measurement, it is well known that the counted value exhibits a Poisson distribution, where the standard deviation of N, $\sigma(N)$, is the square root of the counted value N:

$$\sigma(N) = \sqrt{N} \qquad\qquad \text{...... (1)}$$

The counted value N is the *count rate n* (i.e., the number of counts per second) times the *measured time* in seconds t:

$$N = n \times t \qquad\qquad \text{...... (2)}$$

By applying the rule of error propagation to equation 2, the standard deviation of n, $\sigma(n)$, is expressed as

$$\sigma(n) = \sigma(N)/t \qquad \cdots\cdots\cdots\cdots (3)$$

From equations 1 and 3, we obtain

$$\sigma(n) = \sqrt{(n/t)} \qquad \cdots\cdots\cdots\cdots (4)$$

If the same analyzer and sample are used, the count rate n will be stable; thus the standard deviation will be inversely proportional to the square root of the measurement time (i.e., the length of time the measurements are carried out).

Fig. 10 shows the standard deviation (σ_{n-1}) of measurements of a 1wt% sample with increasing measurement time. The horizontal axis is the measurement time; the vertical axis is the standard deviation. The dots show the actual measured values. For the sake of greater accuracy, measurements were conducted 99 times and the standard deviation obtained. The curve is a proximal straight line with a slope of -0.5. This shows that the results of the actual measurements agree well with the values calculated from the statistical error. Thus it is seen that the SLFA-1800's repeatability can be determined accurately from the statistical error.

The graph in Fig. 11 shows the change in standard deviation according to sulfur concentration. It shows that as the sulfur concentration increases the intensity of the fluorescent X-rays of sulfur becomes greater; and as the value of n in the above equations increases, so does the standard deviation.
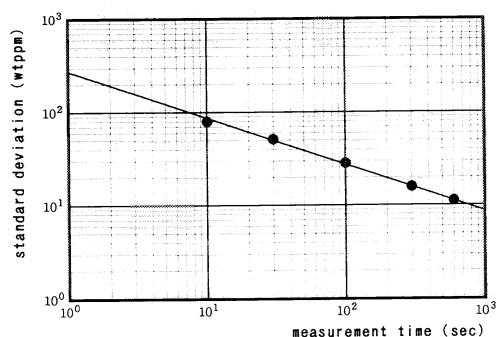

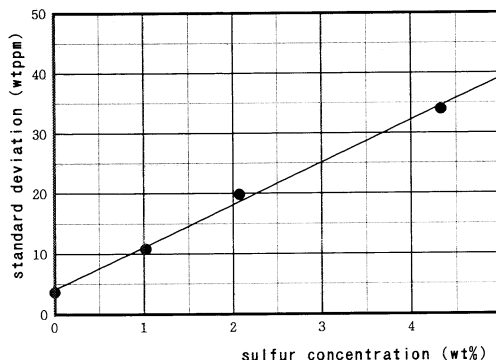**Fig.10** SLFA-1800 performance:measurement time vs. standard deviation

Fig.11 SLFA-1800 performance:sulfur concentration vs. standard deviation

4.2 Warm-up characteristics

In practical terms, one of the important characteristics of analyzers such as this is how they behave when the power is turned on for the first time, i.e., their warm-up characteristics. Naturally, after the device is switched on, the sooner it can be used the better. As with other analyzers, the SLFA Series models do require some warm-up time for the electrical circuits to reach operating temperature. It should also be noted that changes in the temperature of the air in the X-ray path will cause a change in air density, resulting in changes in X-ray absorption.

The SLFA-1800 is equipped with both the temperature correction feature and automatic gain control, described above. These greatly

reduce the required warm-up time. Fig. 12 shows the fluctuation in measurement results occurring with measurements immediately after switching the unit on. The previous model in the SLFA Series, the SLFA-920, needed a warm-up time of about one hour; but with the SLFA-1800, the warm-up time is now close to zero and the unit can be used immediately after it is switched on.
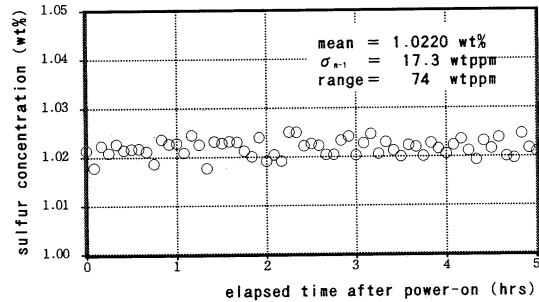

Fig.12 SLFA-1800 performance: elapsed time after power-on and measurement results

### 4.3 Fluctuation in readout values over time

Since the SLFA-1800 corrects for both temperature and atmospheric pressure, not only is the short-time repeatability good, but measurements show improved stability over extended periods of time.

Fig. 13A shows the average value of 100-second measurements repeated three times over a period of 2-1/2 days. A readout was taken roughly every 10 minutes. The standard deviation for the entire data set is 19.4 wtppm, in a range of 119 wtppm. These results clearly demonstrate the stability of readings over extended periods.

Figs. 13B and 13C show the fluctuations in temperature and air pressure during the 2-1/2 day test period. Temperature varied by approximately 4flC; atmospheric pressure varied by approximately 10 mb. Fig. 14 shows the frequency distribution of all the data in this test. The results conform quite well to the normal distribution curve, with no evident examples of aberrant data.
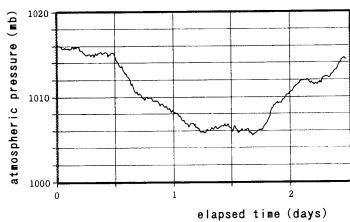
(C) Changes in atmospheric pressure over time
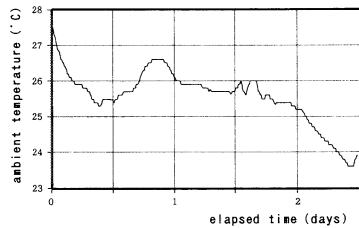
(B) Changes in ambient temperature overtime
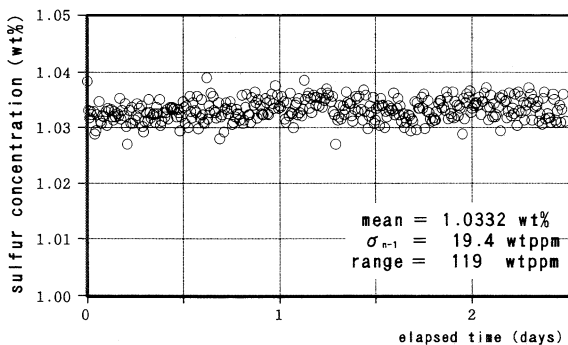
(A) Changes in measurement results over time
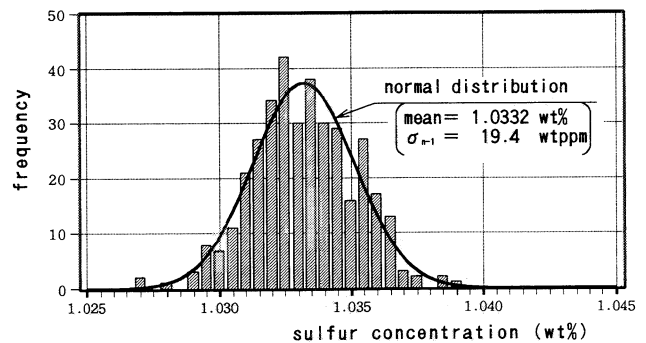**Fig.13** SLFA-1800 performance: long-run stability test results

Fig.14 SLFA-1800 long-run stability test results, expressed as histogram

5. Future developments

Growing concern about environmental problems will be followed by demands for greater precision and accuracy in sulfur measurement. This will call for the ability to measure smaller and smaller amounts of sulfur concentration. As we have seen, to increase measurement accuracy, in principle we must lower the statistical error.

Although it was not discussed in this paper, it should be pointed out that an increase in the X-ray tube output (thus increasing the count rate n), will have the same effect that results from an increase in the length of measurement time. I.e., the standard deviation will decrease in inverse proportion to the square root of the count rate.

Therefore, the easiest way to reduce the statistical error is to strengthen the X-rays. To achieve this we need both a compact, high-output X-ray tube and a new pulse-processing circuit powerful enough to handle the increased count rate of the new X-ray tube. At Horiba we plan to continue our research toward the development of new equipment that can operate at a standard deviation of under 1 wtppm on blank samples.

6. Conclusion

This paper gives a brief introduction to the main features and performance characteristics of the Horiba Model SLFA-1800 fluorescent X-ray sulfur analyzer. There are many factors that have a significant effect on the measurement results in sulfur analysis. Among these are the position of the sample, temperature, atmospheric pressure, the composition of the sample, and the thickness of the sample cell window. All these are crucial questions and deserve to be dealt with separately.

It is hoped that this small essay will be of some help to researchers actively involved in sulfur measurement. Comments or suggestions would be most welcome and should be directed to the author.