IMPROVING THE DETECTION LIMIT IN EDXRF WITH PROPORTIONAL COUNTER

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ABSTRACT

Instruments with the detection limit of 1 to 2 ppm have been designed to satisfy increasing sensitivity requirements in the determination of sulfur in oil and oil products. This can be achieved by the design of instruments and evacuation or He-inletting in a measurement camera. The objective of this work was to design a simple and inexpensive sulfur analyzer based on a gas proportional counter equipped with an air sample chamber and having high sensitivity like many complex instruments. Optimization of the design of the counter and its gas filling as well as development of the filters made it possible to reach 2 ppm detection limit for sulfur determination in oil products.

INTRODUCTION

We have been facing a problem of optimization of all the elements of a simple energy dispersive device to achieve the sensitivity as high as possible when analyzing sulfur and other light elements. A gas proportional counter is cheaper but also has the essential greater dimension of the entrance window, the effectiveness of which for different parts of the spectrum can be varied by choice of a filling gas or its pressure. As is generally known, when the only source of error for an XRF analyzer is a statistical error of the pulses count, the increasing of the sensitivity and the reduction of the detection limit at a constant exposure can be achieved to equal degree both by the increasing of intensity (of the valid signal and the background) and the increasing of contrast (ratio of signal-to-background). Kalinin and Plotnikov [1] shows that in the presence of complementary errors of the measurement, for example when analyzing the oil products under inconstancy of the cuvette film thickness or deflection of the film, the statistical detection limit and the analysis error will be evaluated as these following functional dependencies:

\[ C_{\text{lim}} = 3 \times \frac{\sqrt{B \times T + (A_0 \times B \times T)^2}}{\eta \times T} \]  

\[ \sigma_C = \frac{\sqrt{B \times T + [(A_0 \times B \times T)]^2 + \eta \times C \times T}}{\eta \times T} \]

where \( C_{\text{lim}} \) is the detection limit in %, \( B \) is the count rate of the background sample in pulses/s, \( A_0 \) is the instrument error of measurements in %, \( T \) is the measurement time in s, \( \sigma_C \) is the standard deviation of the predetermined concentration in %, and \( \eta \) is the differential sensitivity \( (\partial J/\partial C)_{C=0} \) (pulses/s per 1 %). Analysis of these formulas and the experimental results confirm
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that the optimal way to achieve the highest possible sensitivity in EDXRF analysis is reduction of the background under the analytical line.

**IMPROVING THE DETECTION LIMIT**

Figure 1 shows spectra of the gas proportional counter pulses from a sample with 0% sulfur concentration (spectrum 1) and with 0.1% sulfur concentration (spectrum 2) in a hydrocarbon matrix. The spectrum is measured on the analyzer ASE-1 [2]. This figure shows the position of the maximum values of the pulse-height distribution for SKα line of the sample and for TiKα line of the X-ray tube anode. It is evident, that in the area of energies corresponding to the S line in a sample, which doesn’t contain sulfur, a noticeable background and a moderate maximum generated by fluorescent radiation of niobium—filter material suppressing air argon radiation—are observed.

![Figure 1. Spectra of the samples with 0% and 0.1% sulfur concentration (Ti-anode X-ray tube; mode of operation: U_{tube} = 8 kV, I_{anode} = 70 µA; Ne/10%CH4 counter gas filling; 30 µm thick Be-window).](image)

For X-ray fluorescent energy dispersive analysis of sulfur without volume evacuation, the following main components of the background have been in place for the energy range to be detected. Low energy component of the X-ray tube radiation scattered on a sample; this component of the background can be suppressed by the filtration of the primary radiation. The emission line ArKα (E = 2.96 keV) was excited by bremsstrahlung and characteristic radiation of the X-ray tube. When performing the analysis in vacuum or He atmosphere, this background component is absent. Fluorescence radiation of the located before detector filter (niobium-filter) was used to pickup the analytical line. The processes associated with the ionization and the charge collection in the counter can also contribute to a low-energy section of the spectrum to be detected. Appearing by the ionization, the photo and Auger electrons carry a part of the energy from the gas amplification area to the cathode counter walls. This result gives the appearance of the pulses analogue to the pulses from the SKα line. For illustration, a typical amplitude distribution spectrum of the Ne/10%CH4-filled counter for a monochromatic line MnKα is
shown in Figure 2. A background constituting approximately 5% of the intensity of the monochromatic radiation is to be observed in 2.3 keV ($S\alpha$) energy range.

Ratio of the maximum intensity of the pulse-height distribution when detecting a monochromatic line to the intensity of pulses at a fixed distance from the maximum is known as peak-to-valley ratio. In this work the peak-to-valley parameter will be determined as the ratio of the intensity near centre of gravity of the amplitude distribution of the $Mn\alpha$ line (in the measurement, an isotope Fe$^{55}$ was used) to the intensity in the $S\alpha$ line area. In a number of works, e.g. in reference [3], a background component resulting from the processes taking place inside of the counter has been examined, and construction and electronics for its elimination have been suggested. We have developed a three-anode proportional counter (Figure 3) and an electronic processing system for counter pulses, which enables us to eliminate pulses attributable to incomplete collection of the photoionization energy. Background counters No. 1 and 3 are included in the counter signal coincidence circuit. It was assumed that the cathode-directed photo and Auger electrons being originated in the basic counter go through the metal grids and come partially to the background counters placed on each side of the main section. When including the background counters in the counter signal coincidence circuit, the pulses corresponding to the incomplete charge collection are excluding from the spectrum, and the ratio peak-to-valley for the basic counter is increasing and the count rate of the pulses on the electronic section output is somewhat reducing.

The electronic systems selecting simultaneity or certain time sequence of the interdependent by some process events (usually particle’s falling into the counters) are well known and are used for nuclear physics. In the developed electronic circuit the analysis is started when the first signal comes from comparators. The delay signal is formed when the time mark coincides with the pulse trailing edge of the comparator. The delay has been controlled in the range from 1.5 to 24 $\mu$s. In the given time interval, the circuit has analyzed the coincidence of the main channel pulses with those of the complementary channels. Failing this coincidence, the circuit has produced the detection signal in the presence of signal from the main channel. In spite of the coincidence analysis in the main and the complementary channels, the circuit has performed a rejection of superposition of pulses in the interval to be studied. The results given below have been received at the duration of the interval to be studied equal to 3 $\mu$s. The tests have shown that in the designed counter using the coincidence system when detecting isotope Fe$^{55}$ radiation, the peak-to-valley ratio has been multiplied by 10 as compared with measurements under the switched-off circuit. But the replacement of the counter in the existent analyzer by the developed three-anode counter and the system gives only 20% reduction of the detection limit. This is because of no change to the above mentioned background components of the argon and filter material fluorescence. To remove this background radiation when analyzing sulfur, evacuation or He-flushing can be used. We sought to avoid the complication of the device and refused that for

![Figure 3. Three-anode proportional counter: 1 and 3 are background counters, 2 is signal (basic) counter, 4 is entrance Be-window, and 5 and 6 are metal grid.](image-url)
sulfur analysis. Slight gain in the detection limit of the sulfur when using the new detector and the coincidence system without evacuation makes their application economically unjustified by the sulfur analysis. However the developed detector and the coincidence system are evidently useful for detection limit reduction of some elements except sulfur. We have chosen the optimal way for the gas-filled proportional counter to increase the sulfur analysis sensitivity without evacuation of the measurement camera volume or He-pumping. The detector design and dimensions and the type of the filling gas have an effect on the background signal values. A set of counters having different design and gas filling has been selected for examination (mixes containing 90% of inert gas and 10% CH₄ have been used). Based on the measurement of the peak-to-valley parameters of the differently designed counters shown in Table I, it is advisable to use Xe-filling counters with larger diameters for the reduction of the detection limit. Let’s compare the effectiveness of the counters with different filling (Figure 4). From the diagram it is evident that the effectiveness of the Xe-filled counter is by an order of magnitude greater in the energy range over 4 keV, where the maximum of the scattered radiation is placed at typical voltages and X-ray tube anode materials. Consequently, the absolute values of the background in the area of SKα are large. We will characterize the combined effect of the peak-to-valley value and the effectiveness of the counter with different fillings on the contrast and detection limit of sulfur by this conventional parameter:

\[ \varepsilon_{rel} = \frac{\varepsilon_L}{\varepsilon_C} \left( \frac{p}{v} \right) \]  

where \( \varepsilon_L \) is the counter effectiveness for the line to be analyzed (in this case SKα) in %, \( p/v \) is the peak-to-value ratio, and \( \varepsilon_C \) is the counter effectiveness at 5.9 keV line (isotope Fe⁵⁵).

From the data in Table I, the values \( \varepsilon_{rel} \) are 2 to 3 times higher when filling with Ne/10%CH₄ for counters of different design and dimensions, despite that for Xe-filling in the experiments with isotope Fe⁵⁵, the peak-to-valley ratio in the sulfur area is appreciably higher. This is because of a low effectiveness of the counters in a short-wave area of the scattered bremsstrahlung spectrum in case of Ne/10%CH₄-filling of the counter when operating with an X-ray tube. In the counters with an output Be-window, the value \( \varepsilon_{rel} \) is higher. It depends evidently on the radiation leakage not to be absorbed in the working space of the counter that creates an additional background by interacting with the cathode. The experiments on evaluation of the sulfur analytical line contrast and sulfur detection limit depending on the use of Xe- or Ne-filling of the counters (Table II) have been conducted with the developed EDXRF Analyzer. The anode power was 0.5 W at a voltage of 7 kV, and the anode material was titanium. Thus, the change of the filling gas and the introduction of the counter output window make it possible to increase the contrast of the SKα
line as well as to reduce by two times the detection limit of sulfur in oil products in comparison with these for the quantity produced sulfur analyzer ASE-1. To achieve the best results when analyzing sulfur in oil products we have examined several ways for sensitivity maximization by improving the excitation conditions for SKα line and reducing the intensity of air argon fluorescence. The material of the X-ray tube anode has been chosen so that its characteristic lines are situated between the absorption edges of sulfur and argon. The material of the primary radiation filter has been chosen so that the absorption edge energy is higher than the energy of the characteristic lines of the anode material. Figure 5 shows the diagram of action of the primary radiation filter made of 1 to 3 µm thick silver.

<table>
<thead>
<tr>
<th>Number</th>
<th>Gas-filling type – pressure, mm mercury</th>
<th>Inner diameter mm/ Be-window thickness, µm</th>
<th>Peak-to-valley ratio (the experiment)</th>
<th>Effectiveness of the radiation detection %</th>
<th>ε_{rel}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ne-700</td>
<td>8,5/30</td>
<td>20</td>
<td>SKα line</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>Xe-550</td>
<td>8,5/30</td>
<td>100</td>
<td>MnKa line</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Xe-550</td>
<td>18/30</td>
<td>150</td>
<td>SKα line</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>Ne-700</td>
<td>18/30</td>
<td>40</td>
<td>MnKa line</td>
<td>91</td>
</tr>
<tr>
<td>5 (2 windows)</td>
<td>Ne-700</td>
<td>18/30</td>
<td>100</td>
<td>SKα line</td>
<td>53</td>
</tr>
<tr>
<td>6 (2 windows)</td>
<td>Ne-700</td>
<td>28/150</td>
<td>130</td>
<td>MnKa line</td>
<td>8</td>
</tr>
<tr>
<td>7 (2 windows)</td>
<td>Xe-550</td>
<td>28/150</td>
<td>180</td>
<td>SKα line</td>
<td>19</td>
</tr>
</tbody>
</table>

Table II. Effect of gas-filling type of a gas-filled proportional counter on analytical characteristic of a light element EDXRF Analyzer.

<table>
<thead>
<tr>
<th>Type of gas-filling</th>
<th>Contrast of SKα line</th>
<th>ε_{rel}</th>
<th>C_{lim} within 600 s (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe/10%CH₄</td>
<td>35</td>
<td>113</td>
<td>0.0015</td>
</tr>
<tr>
<td>Ne/10%CH₄</td>
<td>75</td>
<td>265</td>
<td>0.0010</td>
</tr>
<tr>
<td>Ne/10%CH₄ (2 windows)</td>
<td>100</td>
<td>663</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

The sample radiation excites the air argon fluorescence, the line of which cannot be selected by a gas-filled counter. We have calculated a specialized two-layer filter, being suggested in the work of Plotnikov and Pshenichny [4]. The inner layer, which faces the detector, is made of niobium. The outer layer is PVC film containing approximately 75% chlorine. Both layers absorb the argon radiation and transmit Ka line of sulfur. At the same time the fluorescence in the outer filter, where the greater part of the argon-radiation is transforming, is kept by the inner layer.

On the analogy of the argon fluorescence, the two-layer filter attenuates the L spectrum of silver scattered by the sample and effectively excited the sulfur. This results in multiple reduction of the summary fluorescence of the filter, i.e. essentially reducing background and increasing contrast. The diagram of the position of the absorption edges and the fluorescent lines Ag, Ar, Cl, Nb, and S are shown Figure 6, which illustrates the functioning of the proposed detector.

Use of the silver anode tube, the two-window counter, and the described filters made it possible to reduce the sulfur detection limit in oil products up to 2 ppm, which is comparable with results achieved on more complex and expensive instruments.
REFERENCES


