Application of qualimetric methods for assessing quality of complex products

O P Pudovkin

1 LLC PK MR-Avtomatika, 2A, Voroshilov st., St Petersburg 193318, Russia
E-mail: pudovkin.oleg@gmail.com

Abstract. For the final product high-quality assessment in any application field, it is necessary to choose the optimal method and suitable measuring instruments for the right conditions. The paper reflects theoretical information about the atomic emission spectrometer, the advantages of using this device in the quantitative chemical analysis when monitoring surface waters. In addition, information on methods for evaluating such complex products as the atomic emission spectrometer is provided. The paper presents expert and mixed methods of qualimetry, describes their advantages and disadvantages. Based on them, a new method for evaluating the quality of the atomic emission spectrometer has been developed, which includes elements of the expert method, differential and complex, as well as a method for determining the consistency of experts. In addition, the methodology sets out requirements for experts who are members of the expert group. It is designed such factors as: individual and group weighting factor, assessment of the consistency of experts with the help of the coefficient of concordance, relative indicator of quality, the product quality level, the weighted average arithmetic. Based on the assessment of the last indicator, you can conclude that this product is better or worse than the basic one, or rank several products. Three atomic emission spectrometers were selected for testing this technique. One of them was selected as the base sample, with which the two evaluated samples were compared. They were ranked from best to worst, and their example shows the efficiency of this method.

1. Introduction

The conservation of natural resources and improvement of the environment are priority areas of the government regulated by the Constitution of the Russian Federation. One of the main directions is state monitoring of environmental pollution performed by the Russian hydrometeorological department and other authorized executive bodies of the regions and the State Atomic Energy Corporation Rosatom. When monitoring surface waters, a quantitative chemical analysis of water samples is carried out. P 50.2.090-2013 is used to understand the term quantitative chemical analysis. Quantitative chemical analysis (QCA) involves the experimental quantitative determination (substance, material) of the content (mass concentration, mass fraction, volume fraction, etc.) of one or more components using the chemical, physicochemical, and physical methods [1-4], as well as special measuring instruments [5-6].

When monitoring surface waters in laboratories, selected water samples are analyzed using measuring instruments, which are recorded in the register of approved types of measuring instruments. The purpose of this article is to develop a methodology for assessing product quality...
2. Research object
An atomic emission spectral analysis is a combination of elemental analysis methods based on the study of the emission spectra of free atoms and ions in the gas phase. Usually, emission spectra are recorded in the most convenient optical region of wavelengths from 200 to 1000 nm.

The AES (atomic emission spectrometry) is a method for determining the elemental composition of a substance from the optical emission spectra of atoms and ions of the analyzed sample, excited in light sources [7-9]. Light sources use a burner flame or various types of plasma, including plasma of an electric spark or arc, plasma of a laser spark, inductively coupled plasma, glow discharge, and other nuclear power plants — the most common ones reflect the highly sensitive method for identifying and quantifying impurities in gaseous, liquid, and solid substances, including highly pure ones [10].

The areas of application:
- metallurgy: analysis of the composition of metals and alloys [11];
- mining: research of geological samples and minerals;
- ecology: analysis of water and soil [12];
- Technique: analysis of motor oils and other technical fluids on metal impurities [13];
- biological and medical research [14].

The principle of operation of an atomic emission spectrometer is quite simple. It is based on the fact that the atoms of each element can emit light of certain wavelengths - spectral lines, and these wavelengths are different for different elements. In order for the atoms to start emitting light, they must be excited - by heating, electric discharge, a laser, or some other ways. The more atoms of this element are present in the analyzed sample, the brighter the radiation of the corresponding wavelength is.

Intensity of the spectral line depends on different factors. For this reason, it is impossible to calculate the relationship between the line intensity and the concentration of the element. That is why, standard samples that are similar in composition to the analyzed sample are required. These standard samples are burned. Based on the results of these burns, a calibration graph is constructed for each analyzed element, i.e. the dependence of spectral line intensity of an element on its concentration. In analyzing the samples, these calibration graphs recalculate the measured intensities [15, 16].

Advantages of the method are: lack of contacts; ability to simultaneously quantify a large number of elements; high accuracy; low detection limits; ease of sample preparation; low cost.

3. Quality parameters
When assessing the quality of an atomic emission spectrometer, we attribute the following technical characteristics to the quality indicators: the limit of the working spectral range, nm; spectral resolution, nm; instability of the output signal of the spectrometer, %; limit of a permissible relative error, %; time of establishment of the operating mode, min; power consumption, W; length, mm, width, mm, height, mm, mass, kg; average service life, years.

To evaluate the atomic emission spectrometer by the combined method, all the indicators were divided into individual and group ones. The following indicators are individual ones: instability of the output signal of the spectrometer measuring absolute intensities, the limit of permissible relative errors and the average service life. The first group indicators include the limit of the working spectral range; spectral resolution. The second group includes time of establishment of the operating mode and power consumption. The third group includes length, width, height, and mass. Thus, in the combined method used for assessing quality of the atomic emission spectrometer, three individual indicators and three group indicators are assessed.

4. Quality assessment methods
4.1 Expert quality assessment methods
The expert method is widely used on the basis of generalized experiments aimed to assess the level of product quality (in points) when establishing the nomenclature of quality indicators taken into account at various management stages when determining weighting factors and generalized quality indicators based on a combination of individual and complex quality indicators, as well as certification of product
quality. The main operations of expert assessment are formation of a working and expert groups, product classification, construction of a scheme of quality indicators, preparation of questionnaires and explanatory notes for interviewing experts, interviewing and processing of expert assessments.

To assess the quality of products using the expert method, it is necessary to perform the following operations: to select a range of quality indicators; to create an expert group; to determine the weight of product quality indicators using the preference method; to determine the relative value of product quality indicators; to determine the level of quality by the integrated assessment method; to calculate the integral indicator.

### 4.2 Combined quality assessment method

The combined method is based on the simultaneous use of individual and complex (generalized) indicators of product quality assessment. It is used where the set of individual indicators is quite extensive and the analysis of each of them by the differential method does not allow it to obtain generalized conclusions or when the generalized indicator does not fully take into account all the properties of the product.

It is necessary to combine part of the individual indicators into the groups and determine the corresponding complex indicator for each one; however, some important indicators cannot be combined, but used as individual. Based on the resulting combination of complex and individual indicators, one can evaluate the level of product quality using the differential method.

### 5. The developed methodology for assessing quality and its application

The methodology for assessing the quality of an atomic emission spectrometer consists of several methods for assessing product quality, an expert method, a combined method, and a method for assessing the consistency of experts.

1. An expert group consisting of several experts is formed.
2. The individual indicators of product quality are determined and divided into groups. The group may consist of one indicator or several indicators.
3. The experts provide an assessment $a_{ij}$ for the groups of indicators and individual indicators of the groups.
4. Calculation of group weighting factors $G_i$.
   
   $$ b_i = \sum_{j=1}^{m} a_{ij} $$

   Where $m$ – number of experts, $n$ – number of indicators.

   $$ A = \sum_{i=1}^{n} b_i $$

   $$ G_i = \frac{b_i}{A} $$

5. Calculation of individual weighting factors $a_i$.

   $$ b_i = \sum_{j=1}^{n} a_{ij} $$

   $$ A = \sum_{i=1}^{n} b_i $$

   $$ a_i = \frac{b_i}{A} $$

6. Assessment of the expert consistency using a concordance coefficient $W$.

   $$ \Delta_{ij} = b_i - \bar{b} $$

   $$ S = \sum_{i=1}^{n} (b_i - \bar{b})^2 $$

   $$ W = \frac{m^2 \sum \Delta_{ij}}{12S} $$

   The concordance coefficient $W$ lies in the range from 0 to 1. If the coefficient value is zero, there is no expert agreement, if the coefficient value is 1, the expert opinions are completely consistent.

7. The calculation of the relative quality indicator $q_i$.

   $$ q_i = \frac{P_{asi}}{P_{basl}} $$

   where $P_{asi}$ – the value of the quality indicator, $P_{basl}$ – the value of the quality indicator of the base sample.

8. Calculation of the level of product quality $G_{ijl}$.
\[ G_{\text{TF/E}_i} = \sum_{i=1}^{k} a_i \cdot q_i, \]

9. Arithmetic Weighted Average Calculation \( \hat{Q} \):

\[ \hat{Q} = \sum_{i=1}^{k} G_i \cdot G_{\text{TF/E}_i} \]

10. Assessment of the quality of complex products. By the value of the arithmetic weighted average, you can assess complex products. If the value \( \hat{Q} > 1 \), the evaluated product is better than the base one. Otherwise, the evaluated products are worse than the base one. If we assess several products, we can rank them from the best to the worst ones and vice versa.

6. Application of quality assessment methods

When assessing quality of the atomic emission spectrometer, the following technical characteristics are analyzed: the limit of the working spectral range, nm; spectral resolution, nm; instability of the output signal of the spectrometer, \%; the limit of permissible relative errors, \%; time of establishment of the operating mode, min; power consumption, W; length, mm, width, mm, height, mm, mass, kg; average service life, years.

All these indicators were divided into 6 groups. The first group includes the limit of the working spectral range and spectral resolution. The second group includes instability of the output signal of the spectrometer measuring absolute intensities, and the third group includes the limit of permissible relative errors. The fourth group includes time of establishment of the operating mode and power consumption. The fifth group includes length, width, height, and mass. The sixth group includes the average service life.

Table 1. Calculation of group weighting coefficients and checking the consistency of experts

| Group | Parameter | 1e | 2e | 3e | 4e | 5e | 6e | 7e | 8e | 9e | 10e | bi | A | \( A_i \) | \( \Delta p_i \) | \( \Delta p_i^2 \) |
|-------|-----------|----|----|----|----|----|----|----|----|----|----|----|----|-----------|-----------|-----------|
| 1     | 1,2       | 4  | 6  | 1  | 6  | 4  | 1  | 2  | 3  | 2  | 1  | 5  | 6  | 40        | 0.19       | 19         | 361        |
| 2     | 3         | 3  | 6  | 1  | 6  | 5  | 6  | 1  | 6  | 2  | 5  | 1  | 40  | 0.19      | 19         | 361        |
| 3     | 4         | 4  | 5  | 2  | 5  | 1  | 6  | 5  | 2  | 1  | 3  | 32  | 0.15     | 11         | 121        |
| 4     | 5,6       | 3  | 4  | 2  | 4  | 1  | 3  | 4  | 2  | 4  | 1  | 28  | 0.13     | 7          | 49         |
| 5     | 7,8,9,10  | 1  | 2  | 3  | 6  | 2  | 1  | 3  | 3  | 6  | 2  | 30  | 0.14     | 9          | 81         |
| 6     | 11        | 1  | 2  | 5  | 4  | 3  | 6  | 2  | 5  | 4  | 3  | 60  | 0.19     | 19         | 361        |

Values \( b_{\text{av}} = 21 \), \( S = 1334 \), \( W = 0.74 \), opinions of the experts are agreed, as the value of the coefficient of concordance lies in the range from 0 to 1.

Table 2. Calculation of weighting factors for individual indicators in groups and checking the consistency of experts \( a_i \)

| Group | Indicators | 1e | 2e | 3e | 4e | 5e | 6e | 7e | 8e | 9e | 10e | bi | A | \( a_i \) | \( \Delta p_i \) | \( \Delta p_i^2 \) |
|-------|------------|----|----|----|----|----|----|----|----|----|----|----|----|-----------|-----------|-----------|
| 1     | 1          | 2  | 2  | 2  | 1  | 1  | 2  | 1  | 2  | 1  | 2  | 16 | 30 | 0.53       | 1          | 1          |
| 2     | 1          | 2  | 1  | 2  | 2  | 1  | 2  | 2  | 1  | 2  | 1  | 14 | 0.47       | -1         | 1          |
| 3     | 3          | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 10 | 10         | 1          | 0          |
| 4     | 4          | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 10 | 10         | 1          | 0          |
| 5     | 5          | 1  | 2  | 1  | 1  | 1  | 1  | 1  | 1  | 2  | 1  | 13 | 0.43       | -2         | 4          |
| 6     | 6          | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 1  | 2  | 1  | 17 | 0.57       | 2          | 4          |
| 7     | 7          | 1  | 2  | 1  | 3  | 1  | 2  | 1  | 4  | 3  | 21 | 0.21      | -4         | 16         |
| 8     | 8          | 2  | 1  | 2  | 4  | 1  | 2  | 1  | 2  | 3  | 1  | 19 | 0.19       | -6         | 36         |
| 9     | 9          | 3  | 3  | 3  | 3  | 2  | 3  | 3  | 3  | 2  | 2  | 26 | 100        | 0.26       | 1          |
| 10    | 1          | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 10  | 10         | 1          | 0          |
| 6     | 11         | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 10  | 10         | 1          | 0          |
Values for the groups: 1) $b_{av1} = 15$, $S_1 = 2$, $W_1 = 0.005$; 2) $b_{av2,3,6} = 10$, $S_{2,3,6} = 0$, $W_{2,3,6} = 0$; 3) $b_{av4} = 15$, $S_4 = 8$, $W_4 = 0.018$; 4) $b_{av5} = 25$, $S_5 = 134$, $W_5 = 0.076$. The opinions of experts are agreed, since the values of the concordance coefficients range from 0 to 1.

**Table 3.** Calculation of the relative values of quality indicators

| Indicators | Base sample | $P_{av1}$ | $q_1$ | $P_{av2}$ | $q_2$ |
|------------|-------------|-----------|-------|-----------|-------|
| 1          | 677         | 690       | 1.02  | 650       | 0.96  |
| 2          | 0.5         | 0.6       | 1.20  | 0.4       | 0.80  |
| 3          | 1           | 1         | 1.00  | 0.9       | 1.11  |
| 4          | 20          | 15        | 1.33  | 30        | 0.67  |
| 5          | 30          | 25        | 1.20  | 35        | 0.86  |
| 6          | 1500        | 1500      | 1.00  | 1000      | 0.67  |
| 7          | 2428        | 3000      | 0.81  | 2500      | 0.97  |
| 8          | 1469        | 1376      | 1.07  | 1300      | 1.13  |
| 9          | 1663        | 1408      | 1.18  | 1700      | 0.98  |
| 10         | 60.2        | 60        | 1.00  | 80        | 0.75  |
| 11         | 7           | 6         | 0.86  | 8         | 1.14  |

**Table 4.** Calculation of weighted arithmetic values

| Sample | $G_{T/\epsilon_1}$ | $G_{T/\epsilon_2}$ | $G_{T/\epsilon_3}$ | $G_{T/\epsilon_4}$ | $Q_{w.a.}$ |
|--------|--------------------|--------------------|--------------------|--------------------|------------|
| 1      | 1,10               | 1,00               | 1,33               | 1,09               | 0,86       | 1,06      |
| 2      | 0,89               | 1,11               | 0,67               | 0,75               | 0,93       | 1,14      | 0,93      |

The results of calculations show that the atomic emission spectrometer is better than the base sample or basic atomic emission spectrometer, and the second atomic emission spectrometer is worse than the base one. Thus, it is possible to distribute all three atomic emission spectrometers: 1 - the best, 3 - the worst (Table 5).

**Table 5.** Ranking of assessed atomic emission spectrometers

| Rank | Sample | 1 | 2 | 3 |
|------|--------|---|---|---|
|      |        | Sample 1 | Base sample | Sample 2 |

7. Conclusion

When developing the methodology for assessing product quality, some tasks were performed. The object to be evaluated was an atomic emission spectrometer, which has several characteristics. These characteristics were analyzed as individual indicators of product quality. Due to the fact that the atomic emission spectrometer is a complex product, it is worthwhile to evaluate it using the combined method. The method for assessing product quality and the combined method included elements of the expert differential and integrated method, as well as the method for determining the consistency of experts. In addition, the methodology formulates requirements for experts of the expert group.

When testing the methods for assessing product quality, three atomic emission spectrometers were selected for evaluation. One of them was the base sample with which the two remaining / samples were compared. After the calculation has been performed, the conclusions about the agreement of the experts and quality of the spectrometers were drawn.
References

[1] Nazarenko M Yu, Kondrasheva N K, Saltykova S N 2018 Water and Ecology 1 9-16
[2] Silivanov M O, Vinogradova A A 2019 J. Phys.: Conf. Ser.1384 012067
[3] Saltykova S N, Nazarenko M Yu 2019 Bulletin of the Tomsk Polytechnic University, Geo Assets Engineering 330(11) 172–178
[4] Kondrasheva N K, Rudko V A, Nazarenko M Yu 2018 Coke and Chemistry 61(12) 483-488
[5] Bryukhanov M A, Tsvetkov N V, Vinogradova A A 2018 IOP Conference Series: Earth and Environmental Science 194(6) 062034
[6] Silivanov M O, Vinogradova A A 2019 J. Phys.: Conf. Ser.1384 012067
[7] Nazarenko M Yu, Kondrasheva N K, Saltykova S N 2017 Tsvetnye Metally 7 29-33
[8] Syrkov A G, Sychev M, Silivanov M O, Rozhkova N N 2018 Glass Physics and Chemistry 44(5) 474-479
[9] Nazarenko M Yu, Kondrasheva N K, Saltykova S N 2017 Coke and Chemistry 60(2) 86-89
[10] Grichukha M I, Kremcheev E A 2019 J. Phys.: Conf. Ser.1384 012015
[11] Kondrasheva N K, Rudko V A, Nazarenko M Yu, Gabdulkhakov R R 2020 Journal of Mining Institute 241 97-104
[12] Saltykova S N, Nazarenko M Y 2019 Obogashchennie Rud 5 19-23
[13] Nazarenko M Yu, Kondrasheva N K, Saltykova S N 2018 Coke and Chemistry 61(5) 184-187
[14] Syrkov A G, Silivanov M O, Kabirov V R, Pleskunov I V 2018 IOP Conference Series: Materials Science and Engineering, 387(1) 012076
[15] Boikov A V, Savelev R V, Payor V A, Erokhina O O 2019 CIS Iron and Steel Review, 17 doi: 10.17580
[16] Ushakov I E, Vinogradova A A 2019 J. Phys.: Conf. Ser. 1384 01206