*References*

1. Zimin A. V. Zakrytoe Aktsionernoe Obshchestvo «Nauchno-Proizvodstvennoe Obedinenie "RIVS» — itogi i dostizheniya (JSC "Scientific Production Association "RIVS" — results and achievements). *Gornyi Zhurnal = Mining Journal.* 2012. No. 11. pp. 4–5.

2. Trushin A. A., Sedov A. V., Lyubichenko A. A., Nikandrov I. S. Sistemy avtomaticheskogo regulirovaniya protsessa flotatsii proizvodstva Zakrytogo Aktsionernogo Obshchestva «Nauchno-Proizvodstvennoe Obedinenie "RIVS» (Systems of automatic regulation of flotation process of works of JSC "Scientific Production Association "RIVS"). *Gornyi Zhurnal = Mining Journal.* 2010. No. 10. pp. 69–74.

3. Bondarenko A. V. Variant razvitiya avtomaticheskikh sistem analiticheskogo kontrolya pulp (Method of development of automatic systems of analytical control of pulps). *Gornyi Zhurnal = Mining Journal.* 2010. No. 10. pp. 75–80.

4. Bondarenko A. V., Nikandrov I. S. , Andreev D. S. *«Osobennosti razrabotki RF-kompleksa dlya avtomaticheskogo expressnogo analiza pulp. Tezisy dokladov naychno-practicheskoi konferencii «Nauchno-Proizvodstvennoe Obedinenie «RIVS»* (Features of development of the RF-express complex for automatic analysis of pulps. Abstracts of the scientific-practical «Scientific Production Association «RIVS»). Saint Petersburg. 2014. p. 41.

5. Donald J. Wheeler, David S. Chambers. *Statisticheskoe upravlenie protsessami. Optimizatsiya biznesa s ispolzovaniem kontrolnykh kart Shukharta* (Understanding Statistical Process Control). Translated from English. Moscow : Alpina Business Books, 2009. p. 409.

6. Plekhanov Yu. V., Khmaro V. V., Bondarenko A. V. et al. O sozdanii i ispytaniyakh avtomatizirovannoy sistemy analiticheskogo kontrolya gidrometallurgicheskikh i khimicheskikh protsessov (About creation and tests of automated system of analytical control of hydrometallurgical and chemical processes). *Tezis doklada Pervoy Vserossiyskoy Konferentsii «Analiticheskie pribory»* (Thesis of report of the First All-Russian Conference "Analytical instruments"). Saint Petersburg : Scientific-Research Institute of Chemistry of Saint Petersburg State University, 2002, pp. 144–145.

7. Bondarenko A. V., Gorshkov Yu. V., Karamyshev N. I. et al. K sozdaniyu avtomaticheskikh sistem analiticheskogo kontrolya i ekologicheskogo monitoringa (To the creation of automatic systems of analytical control and ecological monitoring). *Tezis doklada Vtoroy Vserossiyskoy Konferentsii «Analiticheskie pribory»* (Thesis of report of the Second All-Russian Conference "Analytical instruments"). Saint Petersburg : Korona-Print, 2005, pp. 45–46.

8. Bondarenko A. V., Ermakov S. S., Litinskiy A. V. Avtomaticheskoe ekspressnoe opredelenie nizkikh kontsentratsiy elementov v gidrometallurgicheskikh rastvorakh (Automatic express definition of low concentrations of elements in hydrometallurgical solutions). *Tezis doklada Tretey Vserossiyskoy Konferentsii «Analiticheskie pribory». Sbornik «Tendentsii razvitiya analiticheskogo priborostroeniya»* (Thesis of report of the Third All-Russian Conference "Analytical instruments". Collection: "Tendencies of development of analytical instrument engineering"). Saint Petersburg : Russkaya Klassika, 2008, pp. 132–133.

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# X-RAY FLUORESCENT UNIT FOR THE EXPRESS ANALYSIS OF PULP SLURRY

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*The paper describes the development of automatic X-ray fluorescent unit (XFU) intended for the express analysis of pulp slurries, as well as its software, methodical–mathematical and metrological support. It is emphasized that this XFU modification is difficult to implement but is best suitable for mineral processing plants, first of all, for operational control of flotation processes.*

*In accordance with the concept of an automated analytical control accepted by RIVS, the designed automated analytical control system (AACS) is composed of XFU joined with an automated pulp sampling system (APSS) The authors review in brief the functions of the full-scale AACS and its constituents — XFU and APSS.*

*The emphasis is made on the problems and features of XFU with the particular attention given to its analytical and instrumentation characteristics. The designed unit is compared with the best Russian and foreign analogues.*

*The results of the analysis of powder and pulp samples of ore and ore dressing products are presented. It is shown that prime calibration of XFU is possible using model pulps — boric acid-based pellets.*

*Finally, the authors conclude that the designed XFU meets the demands imposed on the express analytical control of ore and ore dressing precuts, and is usable as a prototype for various modifications.*

***Key words:*** *X-ray fluorescent energy-dispersive spectrometer, silicon drift detector, analytical unit, program support, analytical parameters, instrumentation accuracy, methodical–mathematical support, element analysis, pulp slurry products.*

Automated analytical control systems (AACS) have found wide application in mineral mining and processing. Commercial-scale integrated AACS at processing plants are composed of two basic subsystems: an automated pulp sampling system (APSS) including various sampling facilities and an analytical unit (AU) based on X-ray analyzers of powder and slurry samples of ore and ore treatment products.

As a rule, APSS carries out representative sampling, and then delivers and prepares samples for next-following testing for accurate estimation of check characteristics, for instance, composition of elements of pulp solids. Evidently, the express analysis of pulp samples is accomplished by AACS (APSS+AU) as a fully automatic system. In this case, APSS performs automatically all required operations: takes representative point samples, arranges stored samples, actualizes pneumatic transport of the samples, their deaeration, reduction and generation of an express analysis specimen, formation of filtrates of check, shift and inventory samples, and, finally, placement of the express analysis specimen in a measurement flow cell of analytical X-ray fluorescent unit, for instance.

In the framework of the development concept for pulp slurry AACS [1], RIVS has designed, certified and trialed on a commercial scale at processing plants in Russia and other countries different modifications of APSS based on sampling facilities of cross-cut, suction and pressure types [2].

Currently, RIVS carries out research&development aimed at design of proprietary AU based on series-produced X-ray analyzers and using up-to-date components and blocks. In this case, AU is understood as an integrated hardware/software package, including equipment, programming, methodical–mathematical and metrological tools required for the express X-ray fluorescent analysis in computerized and fully automatic modes. The line of AU designed by the Analytical Center of RIVS includes powder, slurry pulp, single-cell and multi-cell modifications of the analytical unit.

This paper deals with a promising option of commercial AU or X-ray fluorescent unit (XFU) for the express analysis of pulp slurries based on a small-size spectrometer with a miniature 4 W X-ray-tube and a latest detector of SDD type (Silicon Drift Detector). These components were purchased at the known Amptek company (USA), whose achievements in the area of the modern energy-dispersive spectrometers and semiconductor detectors are widely used by NASA. It should be mentioned that most hardware constituents of AU, including those manufactured by Amptek, are supplied either without software support, or with the software for only manual operation under laboratory conditions.

It only appeared technically complicated to integrate all constituents of AU and adapt them to smooth round-the-clock automatic operation as a part of AACS at a processing plant.

At the present time, the Analytical Center of RIVS trials the prototype single-cell and multi-cell pulp XFU as the most challenging option in terms of implementation. It is worthy of emphasizing that such type of AU was designed based on the advanced hardware and software and know-how elements included in the program-algorithmic, methodical–mathematiucal and metrological support, and is now at the sage of licensing.

The software environment developed for AU has a modular user–server architecture that allows on-the-fly optimization and expansion of functionals (**Fig. 1**).

The modern technologies and know-how elements used in the software environment design condition:

- simplicity of operation — AU is idiot-proof, and properly set AU needs minimal operator's control;
- extended self-diagnostics capacity — operation of all subsystems is logged, up-time and down-time are recorded, procedure validity is controlled and relevant error messages are created, i.e. the system informs on malfunctions and calls for suitable maintenance;
- simplicity of maintenance support — AU constituents are designed for long-term operation, which, together with the self-diagnostics capacity, enables reduction in operating cost;
- various alternatives of setting, control and monitoring — it is possible to use both in-built display facilities (operator's board) and any other computers via Web-browser or SCADA system;
- extended integration of AU in intelligent systems of a plant — AU can be operated by means of discrete signals, OPC (OLE for Process Control) or API (Application Programming Interface), and AU data can be taken from files, data bases or Web-pages using OPC or API;
- functioning of AU as a part of AACS — AU was initiated for the use as a part of a full-scale AACS for pulp slurries and dressing products, and it was anticipated that a number of AU could operate concurrently with APSS.

All in all, most advantages and constraints of the similar operating systems were taken into account in the AU design in order to comply with the modern requirements imposed on analytical, operational and economic characteristics of XFU [3].

Capabilities of the developed AU were estimated using procedures from [4, 5]. For example, the estimate of the analytical characteristics of the unit included measurements taken on model solutions — samples of 1% of check elements in boric acid ($H_3BO_3$).

**Table 1** gives the calculated concentration sensibility, detection level and dead time.

One of the basic characteristics of the detector is its energy resolution. In the semiconductor detection technology, this characteristic is in close relationship with the other two characteristics represented by the counting rate and dead time. **Fig. 2** illustrates the relationship between the energy resolution, counting rate and the dead time in the line of MnK$\alpha$ (5.9 KeV).

The measurement results shown in Fig. 2 were obtained on a state standard specimen (SSS) represented by an alloy with the content of Mn 14%. The counting rate was increased by raising the X-ray tube amperage.

The prototype XFU was tried in terms of short-term and long-term consistency of operation. As XFU was intended for

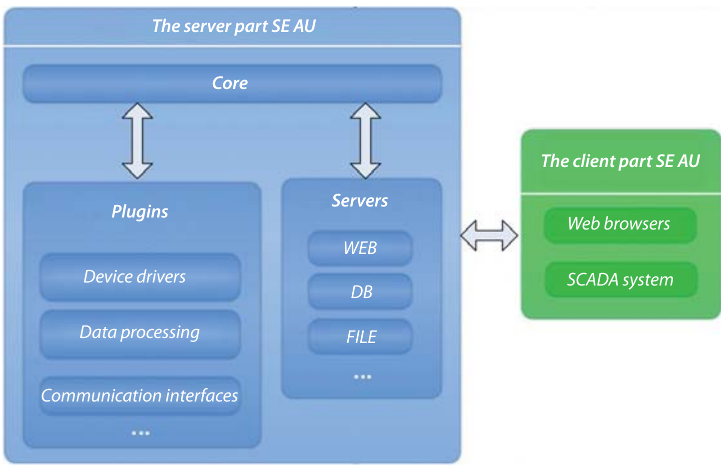


**Fig. 1. Generalized structure of software environment for AU**

**Table 1. Analytical characteristics of AU**

| Check element | Concentration sensibility η, pulse/s/% | Detection level *L*, ppm | Dead time, % |
|---|---|---|---|
| Mn | 780 | 7 | 9.6 |
| Fe | 1749 | 5 | 8.9 |
| Co | 1534 | 4 | 10.5 |
| Ni | 5178 | 2 | 10.3 |
| Cu | 4539 | 2 | 10.0 |
| Zn | 6805 | 2 | 10.6 |
| Pb | 6520 | 5 | 10.9 |
| Mo | 23556 | 4 | 16.2 |

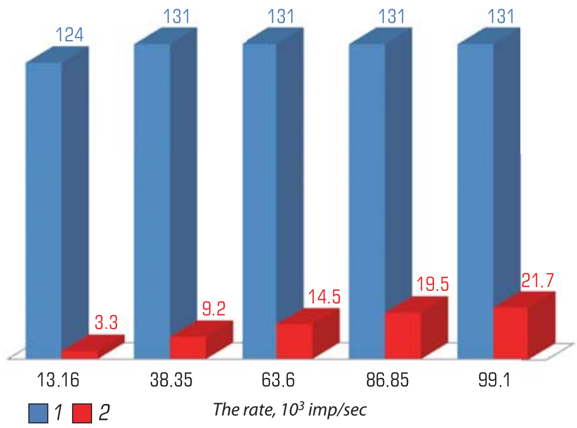


**Fig. 2. Relationship of the energy resolution counting rate and the dead time in the line of MnKα (5.9 KeV):**
*1* — resolution, eV; *2* — dead time, %

continuous commercial operation, of interest was first of all the long-term operation consistency.

The long-term (24 hours of continuous operation) accuracy of AU instrumentation was estimated using a metal alloy and sampled pulp slurry of complex ore.

The instrumentation accuracy estimation conditions were as follows:

- X-ray tube voltage—40 kV at 70 µA;
- "window" constructed by the analytical lines of MnK , FeKα, CuKα, ZnKα, PbLα enclosed almost 95% of amplitude distribution peak;
- exposure time — 100 s;
- pulp slurry flow in a circulation loop — 18 l/min;
- film of the measurement cell (for pulp slurry) was made of polyethylene terephthalate 20 µm thick;
- measurement frequency — 1 at every new position of the spectrometer block on the cell with the solid specimen or the pulp slurry sample.

The measurement of the intensities of the analytical lines on the alloy specimen and the pulp slurry sample, along with the principal instrumentation accuracy A0, governed by drift of the spectrometer characteristics, and the theoretical statistical pulse counting error Vpc, included the complementary error due to non-reproducible positioning of the spectrometer block relative to the measuring window of the cell. Furthermore, the measurement taken on the pulp slurry sample added the overall instrumentation accuracy $A_\Sigma$ with the error due to the circulation loop, $V_{cl}$.

The principal instrumentation accuracy was estimated based on the measurements taken on the metal specimen, while the overall accuracy was estimated using the pulp slurry sample in accordance with the procedures described in [4]. The measurement results are compiled in **Table 2**.

As seen, with the metal specimen, $A_0$ varied from 0.12 to 0.37% for different analytical lines. These values calculated by the procedure of estimation of $A_0$ (with the statistical component neglected) give an acceptable characteristic of long-term drift of AU instrumental parameters. The overall instrumentation accuracy of the measurements on the pulp slurry sample (without regard for Vpc) ranged between 0.42 and 1.1%, and the main contribution in $A_\Sigma$ is made by the circulation loop with the flowing heterogeneous medium under measurement. The theoretical statistical error $V_{pc}$, depending on exclusively total

**Table 2. Calculated principal and overall instrumentation accuracies of AU for 24 hours of continuous operation**

| Line | Metal specimen | | | Pulp slurry sample | | | |
|---|---|---|---|---|---|---|---|
| | Counting rate, pulse/s | $A_0$, % | $V_{pc}$, % | Counting rate, pulse/s | $A_\Sigma$, % | $V_{pc}$, % | $V_{cl}$, % |
| MnKα | 105 | 0.19 | 0.98 | 113 | 0.6 | 0.94 | 0.57 |
| FeKα | 402 | 0.37 | 0.5 | 1117 | 0.42 | 0.3 | 0.2 |
| CuKα | 1661 | 0.21 | 0.25 | 93 | 0.97 | 1.04 | 0.95 |
| ZnKα | 458 | 0.23 | 0.47 | 618 | 0.48 | 0.40 | 0.42 |
| PbLα | 170 | 0.12 | 0.77 | 629 | 1.1 | 0.40 | 1.09 |

Comment: the metal specimen composition, %: 0.36 Mn; 1.04 Fe; 1.38 Cu; 0.21 Zn; 0.12 Pb; the pulp slurry sample composition, %: 30 — solid phase; elements in the solid phase: 0.64 Mn; 7.05 Fe; 0.22 Cu; 1.02 Zn; 3.11 Pb.

**Table 3. Element detection level, ppm**

| Equipment, manufacturer, country | X-ray tube wattage, W | Anode and X-ray tube modes | Element | | | | |
|---|---|---|---|---|---|---|---|
| | | | Cu | Zn | Pb | Ni | Fe |
| AU, RIVS, Russia | 4 | Ag (40 kV, 70 µA) | 2 | 2 | 5 | 2 | 5 |
| S2 RANGER, BRUKER, Germany | 50 | Rh (40 kV, 200 µA) | 3 | 5 | 12 | 3 | 4 |
| SRM-13, Burevestnik SPA, Russia (data from [5]) | 2000 | Pd (50 kV, 40 µA) | 2 | — | — | 2 | 5 |

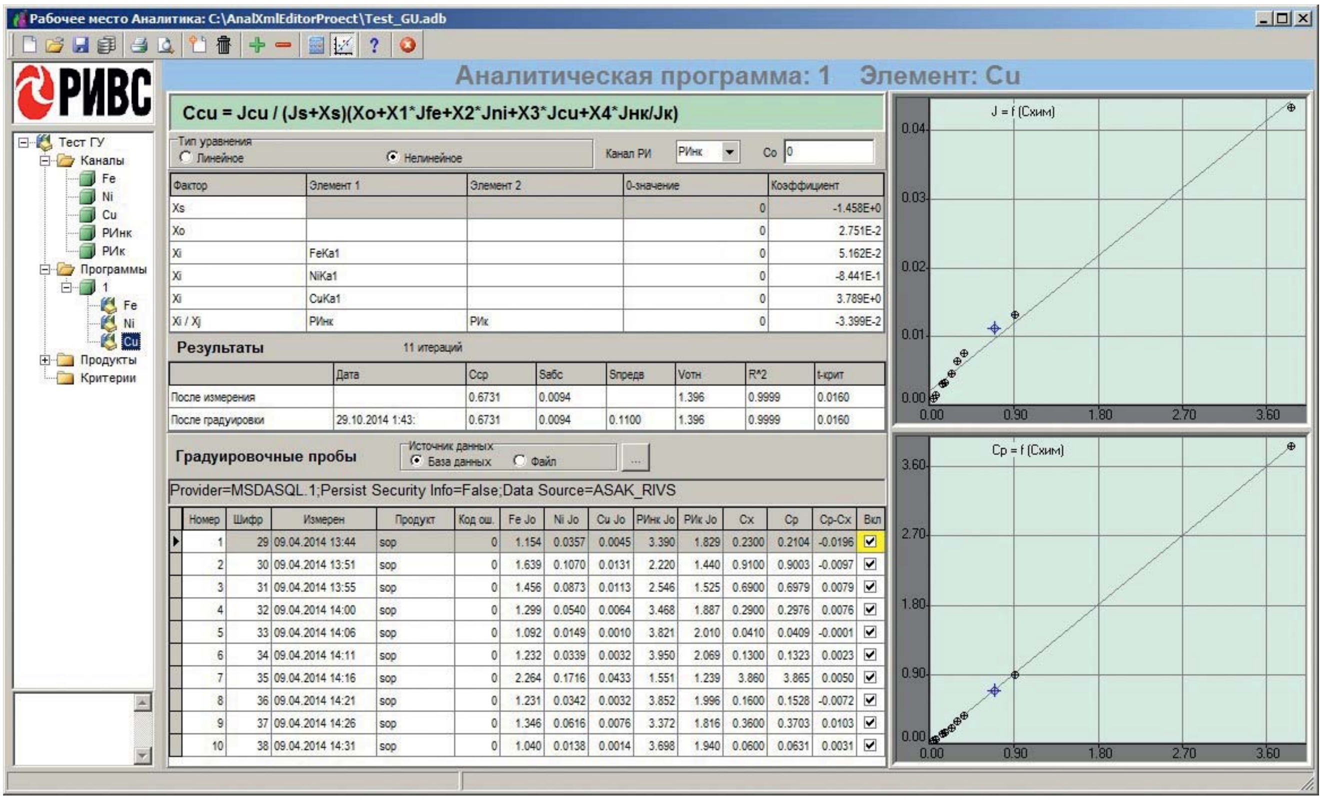


**Fig. 3. AWP Analitika program, main window: XFU calibration results for the content of Cu in powder samples of a copper–nickel ore state standard specimen**

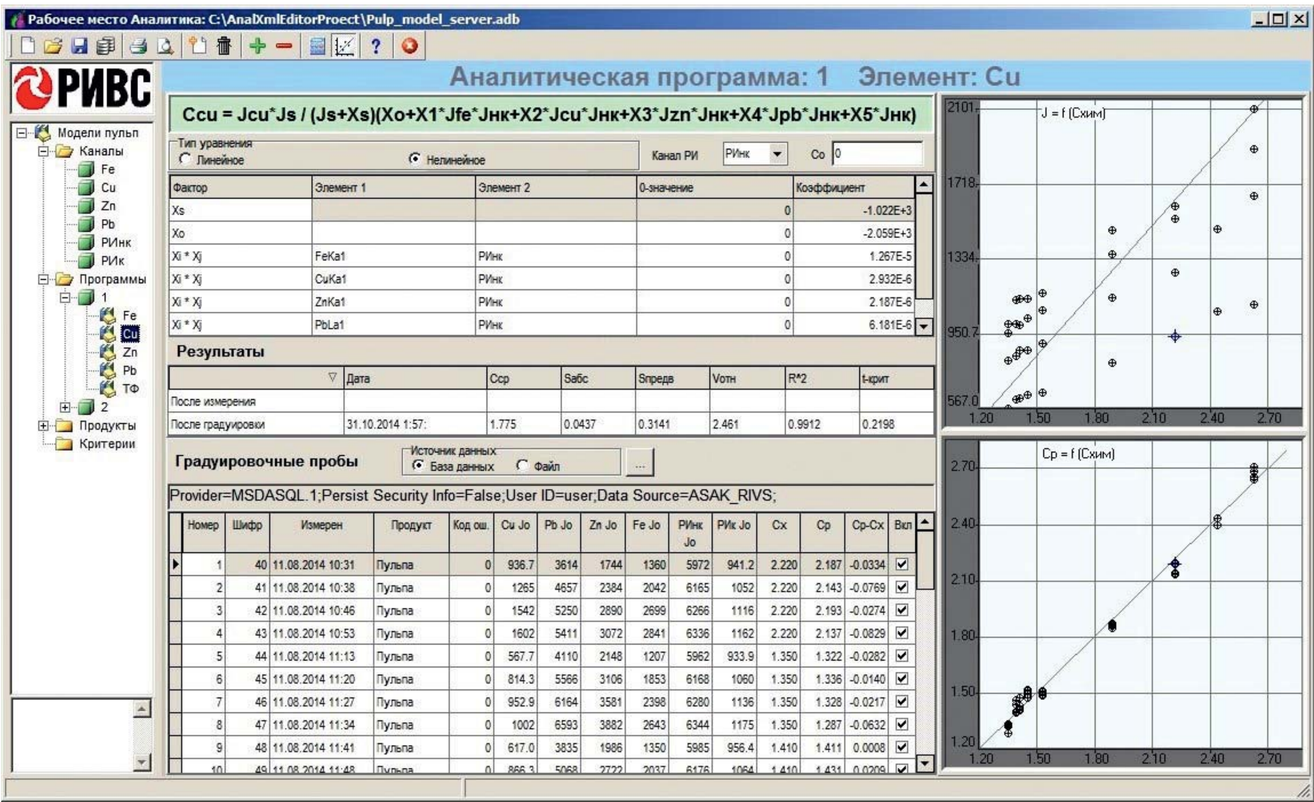


**Fig. 4. AWP Analitika program, main window: XFU calibration results for the content of Cu in the solid of pulp slurry based on measurements taken on model pulps ($H_3BO_3$-based pellets)**

**Table 4. Test of the coupling equations obtained on model pulps by estimation of content of elements in solid phase of actual pulp slurries**

| Element | Cs = 5–40% | | |
|---|---|---|---|
| | $\bar{C}$, mass percentage | S p-x, mass percentage | V p-x, relative percentage |
| Cu | 1.32 | 0.10 | 7.6 |
| Zn | 2.06 | 0.14 | 6.8 |

set of pulses within the exposure time, had relatively high values in the case discussed since the specimens with low content of the check elements were purposely used.

As against one of the Russia's best X-ray units based on spectrometer SRM-13 for pulp flow analysis, the designed AU yields the values of the overall instrumentation accuracy for continuous 24-h operation that are comparable with the values of the instrumentation accuracy estimated by SRM-13 for 4 hours of continuous measurement [4].

The described research also compared the detection levels of the designed AU and the front-rank energy-dispersive and wave-dispersive XFU featuring high analytical performance. The measurements were taken on model solutions of 1% of a check element in boric acid. **Table 3** presents the obtained detection levels for some of the check elements.

Based on the evidence of Tables 2 and 3, the designed AU possesses high analytical and instrumentation characteristics meeting the demands imposed on X-ray fluorescent units in accord the formulations in [3].

The Analytical Center, RIVS had developed the up-to-date AWP Analitika program based on the unified methodical–mathematical support for research and calibration measurement using powder and pulp slurry specimens and various mathematical models and algorithms [6]. **Fig. 3** offers an illustration of AU capacity in detection of elements in compound heterogeneous media represented by ores and ore dressing products.

The nonlinear calibration equation (refer to Fig. 3) adequately relates the measured intensities of analytical lines and scattered (coherently and incoherently) characteristic radiation of X-ray tube anode with concentrations of the check element Cu in the powder SSS of copper–nickel ore. Indeed, the coefficient of determination, $R^2$, describing relative measure of agreement, is 0.9999, and an absolute measure of agreement, that is a mean-square difference between the X-ray spectral concentrations of Cu and the Cu concentrations reliably estimated using a chemical method at the average value ($\bar{C}$) of 0.67 mass percentage, is 0.009 mass percentage ($S_{p\text{-}x}$) or 1.3 relative percentage ($V_{p\text{-}x}$).

The pulp XFU was used for testing model pulps — boric acid-based pellets and actual pulp slurry samples with the content of solid (Cs) from 5 to 40 mass percentage. By way of example, **Fig. 4** shows the calibration results for pulp slurry models, and **Table 4** presents the outcome of the test of the coupling equations obtained for the actual pulp slurry samples.

As follows from Table 4, even at high fluctuation of the content of solid in pulp slurry and with the pulp slurry models used in the calibration, the X-ray fluorescent unit yields acceptable estimates of the content of elements in the solid phase of the actual pulp slurries.

Generally, the research findings imply that the analytical and instrumental characteristics of the designed equipment allow handling a variety of problems associated with the express analytical control in mineral mining and processing. Moreover, it enables prime calibration prior to introduction of the pulp XFU at a plant with the next-following adjustment of the coupling equations in the course of the unit operation.

*References*

1. Bondarenko A. V. Variant razvitiya avtomaticheskikh sistem analiticheskogo kontrolya pulp (Method of development of automatic systems of analytical pulp control). *Gornyi Zhurnal = Mining Journal.* 2010. No. 10. pp. 75–80.

2. Bondarenko A. V., Zakharov P. A., Nikandrov I. S., Smirnov S. A., Shevelev E. S. Razrabotka avtomatizirovannoy sistemy oprobovaniya pulpovykh produktov (Development of automated system of pulp products testing). *Tezisy dokladov nauchno-prakticheskoy konferentsii Nauchno-Proizvodstvennogo Obedineniya «RIVS»* (Thesis of reports of scientific-practical conference of Scientific Production Association "RIVS"). Saint Petersburg, 2012, pp. 35–36.

3. R. Kellner, J.-M. Mermet, M. Otto, H. M. Widmer. *Analiticheskaya khimiya. Problemy i podkhody* (Analytical chemistry. Problems and approaches). Moscow : Mir, 2004. Vol. 2, p. 726.

4. Bondarenko A. V. Apparaturnye pogreshnosti pri rabote rentgenovskogo analiticheskogo kompleksa SRM-13-EVM ASVT M-6000 (Implementation error in the time of operation of X-ray analytical complex SRM-13-EVM ASVT M-6000 (СРМ-13-ЭВМ АСВТ М-6000)). *Apparatura i metody rentgenovskogo analiza* (Apparatus and methods of X-ray analysis). Leningrad : Mashinostroenie, 1982. Iss. 27, pp. 39–42.

5. Bondarenko A. V. Ispolzovanie rentgenovskogo kompleksa SRM-13-EVM M-6000 dlya analiza produktov obogashcheniya medno-nikelevykh rud (Use of X-ray complex SRM-13-EVM M-6000 (СРМ-13-ЭВМ М-6000) for analysis of copper-nickel ore concentration products). *Apparatura i metody rentgenovskogo analiza* (Apparatus and methods of X-ray analysis). Leningrad : Mashinostroenie, 1984. Iss. 32, pp.99–104.

6. Bondarenko A. V., Karamyshev N. I., Katsman Ya. M. Nelineynoe otsenivanie parametrov v inzhenernoy praktike Zakrytogo Aktsionernogo Obshchestva «Nauchno-Proizvodstvennoe Obedinenie RIVS» (Non-linear assessment of parameters in engineering practice of JSC "Scientific-Production Association "RIVS"). *Gornyi Zhurnal = Mining Journal.* 2011. No. 10, pp. 73–78. EM

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