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THE ROLE OF ZIRCONIUM IN 21ST CENTURY TECHNOLOGY

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Annotation

Zircon plays an important role in the modern economic life of Uzbekistan. First, in terms of zirconi um mineral reserves, Uzbekistan is one of the world's leading countries and the fifth largest among the CIS countries. Second, the metal zirconium is the basis of the structural (filler metal) material for the core of nuclear reactors. In the 21st century, Uzbekistan will make a significant contribution to the development of nuclear energy. According to current forecasts, the launch of production of zirconium alloys for the planned nuclear power plant in Uzbekistan after 2022, a new generation of zirconium alloys will play a decisive role in the future of promising nuclear and fusion reactors. In Uzbekistan, the development of the country's economy through the processing of zirconium ores is planned to launch the production of zirconium metal. Third, chemical engineering could become the second application of zirconium after nuclear power, due to its resistance to corrosion in aggressive environments. In the chemical, food and pharmaceutical industries, the replacement of metallic and non-metallic stainless alloys with zirconium materials is not only economically viable, but in many cases technically feasible. In ferrous and non-ferrous metallurgy, it is traditional to use zirconium to improve the performance and modification of structural steels, to improve the quality of copper, aluminum, magnesium and other alloys, and in some cases to replace rare and toxic metals.

1.1 Introduce the Problem

Modification with zirconium leads to an increase in cast density and increases the corrosion resistance of bronze. ZrCu intermetallic compound is a catalyst for the synthesis of methanol from monoxide and hydrogen is

Cathodes made of commercially pure zirconium in the form of cylindrical or conical products and ZG-20 alloy of zirconium are used to place durable nitride coatings on tools and gas turbine blades according to the CIB method. At the same time the durability of products increases by 3-4 times.

Zirconium tetrafluoride is a starting material for obtaining high purity substances of optical fiber. This is not an exhaustive list of uses for products made of metallic zirconium and its alloys.

The main directions of consumption of metallic zirconium:

1. Atomic energy (fuel cells in nuclear reactors due to low absorption cross section of thermal neutrons and good corrosion resistance) and channel pipe shell as);

2. Chemical-technological equipment and aerospace industry production (Cl_2, HCl, alkali and high solubility, corrosion resistance due to);

3. Manufacture of ferrous metallurgy and various alloys remove

To obtain zirconium in nuclear purity, it is necessary to open the concentrate, enrich it, separate unnecessary impurities, separate zirconium and hafnium. The final product that can be returned to the metal is ZrO_2, $ZrCl_4$, ZrF_4, K_2ZrF_6. Let’s take a look at the main ways to get and clean these compounds.

Various methods can be used to separate zirconium and hafnium, including fractional crystallization and precipitation, fractional distillation and sublimation, ionization, chromatographic method, liquid extraction, and more.

In Canada and India, extraction is carried out from Nitrate solutions of TBP. In Canada, the zirconium nitrate solution obtained after extraction and re-extraction processes evaporates and is converted to the tetrafluoride form before zirconium is returned.

1.2 Explore Importance of the Problem

1. The choice of separation method is determined by the methods used to break down and mine the ore, as well as the availability of the necessary structural materials. Zirconium and hafnium are separated from free acidic solutions to prevent hydrolysis. In these processes, zirconium-hafnium tetrachloride is dissolved in a free solution containing SCN ion added in the form of NH4SCN. Methyl isobutyl ketone (hexane) is pre-saturated with HSCN thiocyanate at a concentration of 1-2 M, contacting it with a solution of sulfuric acid of NH4SCN. the zirconium solution obtained by melting is given for extraction with methyl isobutyl ketone, which selects hafnium, while remaining. in the water phase. The extraction process is carried out on irrigated columns. Refined sulfuric acid containing sulfur-free zirconium is precipitated as a sulfate complex in the form of Zr5O8 (SO4) 2, precipitated at a certain temperature and pH, the precipitate is filtered, filtered, washed, ammonia. hydrated Zirconium is obtained, which is then chlorinated to obtain a non-galvanic ZrCl4. To reduce the iron content, pure zirconium tetrachloride is sent to sublimation in a hydrogen atmosphere. The method of separation of zirconium and hafnium by liquid extraction has a number of drawbacks:

2. Nitrates and organic substances in the process of liquid extraction Significant amounts of liquid waste are generated with traces, which is a difficult task to remove due to the strengthening of environmental protection requirements. The problem is that the consumption of chemicals in the extraction process is high and requires complex and corrosion-resistant equipment is done.

3. It was not practical or economical to first obtain anhydrous Zirconium tetrachloride, convert it to an aqueous solution, purify the zirconium by liquid extraction from hafnium, and then return it to anhydrous $ZrCl_4$ before proceeding to the reduction phase . In addition, the obtained $ZrCl_4$ and $HfCI_4$ can be purified to remove oxygen and nitrogen from them, as well as iron and aluminum. Need of pure $ZrCl_4$ relative to technical ZrC is 70- 80%. Currently, zirconium and hafnium are separated by sublimation of hafnium tetrachloride in one of the US plants . This process involves heating $HfCl_4$, Zirconium tetrachloride at 400 ° C in an inert gas atmosphere with Zirconium powder or ZrC. $ZrCI_4$ is converted to non-volatile $ZrCI_3$. Hafnium tetrachloride is not recoverable and cannot be sublimated with non-reactive $ZrCl_{4\,.\,An}$ imbalance occurs when $ZrCI_3$ is heated to 450 ° C ($2ZrCl_3 \Rightarrow ZrCl_4 + ZrCl_2$). The tetrachloride is sublimated and the non-volatile dichloride is used as a reducing agent in the next cycle.

The main focus in improving the separation of zirconium and hafnium was to create a continuous process for the direct separation of $ZrCl_4$ and $HfCl_4$. Studies with dissolved salts, including zirconium tetrachloride, have shown that ZrCI can be theoretically separated. By distillation of $ZrCl_4$ and $HfCl_4$ in a solution of dissolved salts at a pressure of 1 kg*s/cm^2 by adding a mixture of $ZrCl_4$-NaCI-KCl to a solution of $ZrCl_4$ / $HfCl_4$ with no impurities . After the initial $ZrCl_4$ / $HfCl_4$ mixture is completely dissolved, the solution is sent to a column for thermal distillation, from which a sufficiently pure hafnium tetrachloride is obtained as a higher fraction, which is used for subsequent reduction . the resulting lower fraction is removed from the column and high-purity $ZrCl_4$ vapors are obtained from the eutectic mixture, which are suitable for recovery by evaporation. The molten eutectic is returned to the beginning of the process. Eutectic temperature is ~ 218° C.$HFCI_4$ parts are mixed with NaCl and COP to obtain a secondary eutectic solution. In this connection, it is necessary to remove from the system a portion of the solution which can be given directly to a reduction apparatus containing a mixture of magnesium or potassium and sodium, and to obtain metal zirconium.

Japanese experts have patented a method of purifying ZrCl 4 containing HfCI 4 , fractional thermal distillation in columns, and $ZrCl_4$ is obtained from the lower part of the low corrugated column and high corpus $ZrCl_4$ from above. The process consists of several operations:

1) one outer surface of the column from $ZrCI_4$ sublimation temperature, heating the latter below the sublimation temperature;
2) technical $ZrCl_4$ vapors to low temperature surfaces to give;
3) removing condensate from the high temperature surface throw away
4) a warmer surface of a portion of the condensate to form vapors contact to do;
5) repeat the condensation process and obtain $ZrCI_4$ vapor.

The results of the study and extraction-chromatographic separation of Zr and Hf in nitric acid solution with solid extractant (TSEX) based on tributylphosphate (TBP) are presented.

In TVEX, the TBP content was 65%. The research was carried out in a laboratory on a thermostatic column with a cross-section of 1.41 cm^{2}, the height of the TVEX layer was 11.0-22.0 cm, the metal concentration was 1.0-5.2 g/l, the temperature of the solution. It was 40°C. The separation coefficient of Zr and Hf was 3.9. During the experimental tests, a thermostatically controlled pressure column with a height of 3.10 m was used. Complete the layer of estragent The cleaning took place after 135 hours.

Data on extraction of Zr and Hf from nitric acid solutions with an increasing amount of tributylphosphate with a solid extractor (65%) and the results of experimental tests on extraction from pulps containing large amounts of SiO_2 listed. Equilibrium, kinetics, aqueous acidity, and the effect of temperature on the process were studied. Similarities with liquid extraction have been noted. An increase in extractor capacity for both metals was noted with increasing temperature. The enthalpy of the process is determined graphically. Approximately 90% Me was passed into the solution during the re-separation of Zr from the solid extractant for 30 ... 40 min.

NH_4HF_2 belongs to the type of clay and contains (%) ZrO_2-52.09; SiO_2-45.35; Al-0.45; Fe-0.16; W-0.2; Hf ~ 1 and more than 20 elements have been studied by the authors.

The following technological parameters are recommended for opening the concentrate: temperature 25-170°C, time (at 80 ° C for 10-15 kg mass) 36 hours, consumption of 1 ton of concentrate NH_4HF_2 – 1.65 tons. In molar ratios over a wide range and different temperatures instead to be increased mutual effect kinetics of the process study.

A chloride method was proposed to process Zircon sands by separating Zr and Hf. The ore is chlorinated. Exhaust gases pass through a condenser in which the main components are deposited and the most volatile 51 STs are separated. Chloridose condensate is treated with an acidic solution at pH 1 ... 3 to dissolve Zr and Hf. By raising the pH of the separated solution to 3 ... 7, U precipitate is formed. The residue from chlorination is washed with acid, the caprochlorinated Me residue is removed. The solution contains Ba, Ra and Pb sulfates sink for SO_4 or appropriate carbonates sink treatment with CO_3

2- for is given.

The article deals with the processing of Far Eastern mineral raw materials using the latest ammonium bifluoride-based technologies. the problem is considered. The possibility of producing ammonium bifluoride from fluorite mined in the village of Yaroslavskiy is based on. The most important feature of fluorine metallurgy is the production of high-purity metallurgical products directly from concentrates reported.

The method of complex processing of fine-grained zirconium-ilmeite sands is patented. From the stoichiometry of the decomposition reaction of Ti-minerals with the addition of ammonium sulfate up to 15 W, the collective concentrate is separated into Zr, Ti, rare and REM-compounds by sulfation in excess of 3- 30% of sulfuric acid 15%, then diluted with water and isolation of filtrate and cake target products. Sulfation is carried out at 180-240 ° C.

The Atomic Center (India) has developed and put into production the entire technological scheme, from mining to the production of metal zirconium and the production of alloy components. Work was carried out to improve all stages: washing, chlorination, magnesium-thermal, distillation, iodine purification. It is suggested to turn it into a powder by processing. Zr-Al alloys for the production of high-strength AI for receivers.

The history of the development of zirconium metallurgy is reviewed by the Mines of Bureau in Albania. The work summarizes the results on vskra. Concentrations of zirconium, separation of zirconium and hafnium, reduction of zirconium oxide, reduction of zirconium to metal. Theoretical and experimental data were systematized.

Thermal decomposition of compounds, hydrometallurgical methods of separation of zirconium and hafnium, cir chlorides have been developed and used. Iodine and electrolytic IU. Purification of zirconium and hafnium.

The following soda-extraction technology processes are used in PCZ to obtain pure zircon tetrachloride. Discovery of zircon concentrate.

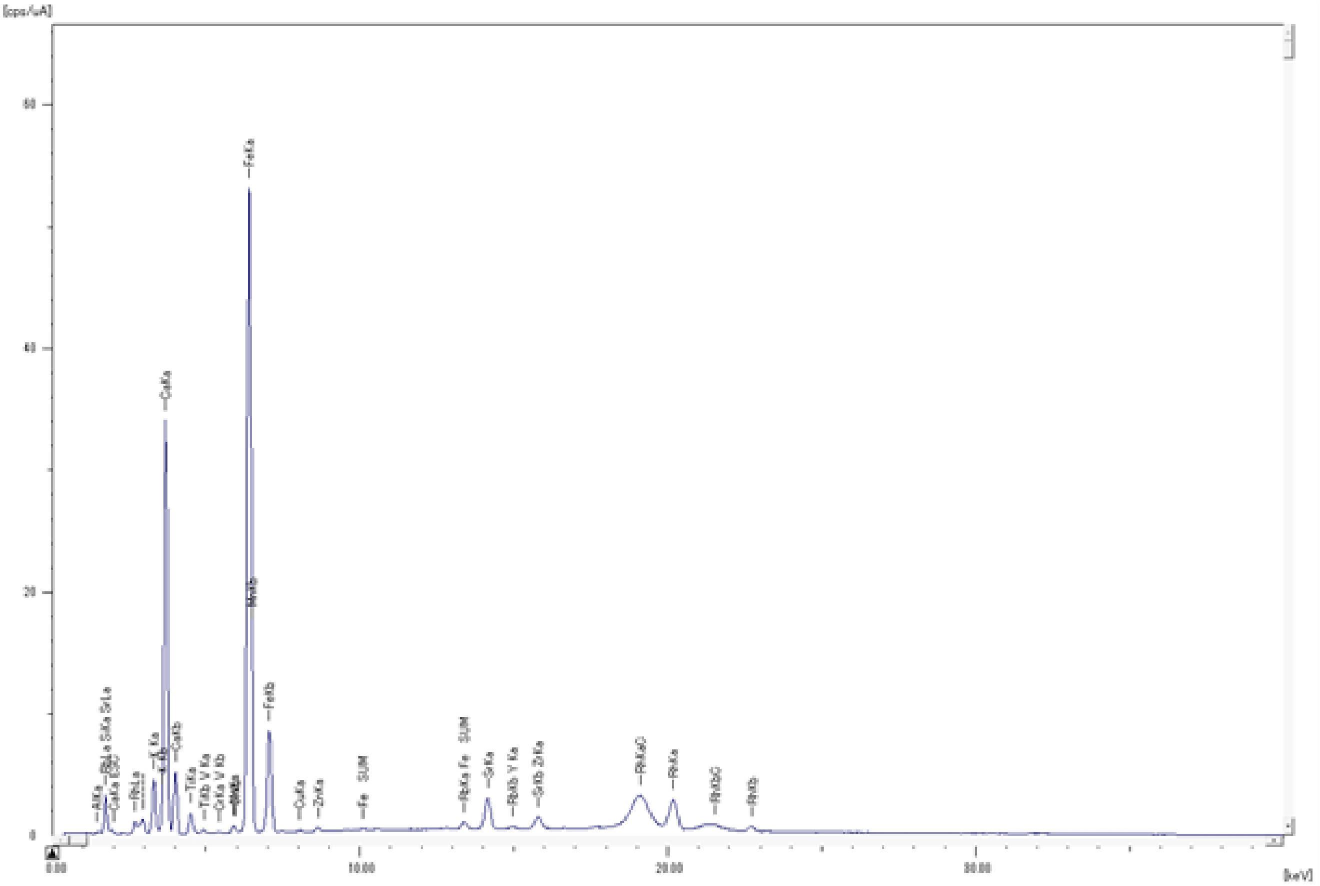
In the fields of Ukraine. Zircon opens with a combination of caustic. Soda at high temperature. The resulting opening of the solution containing sodium zirconate is washed with water, soda and sodium silicate. High buffer type furnaces are used for opening. Furnaces are protected, continuous melting zirconium ceramics. The heating of the reaction mass is carried out due to the heat emitted by the electrodes. The process is carried out in the following cases.

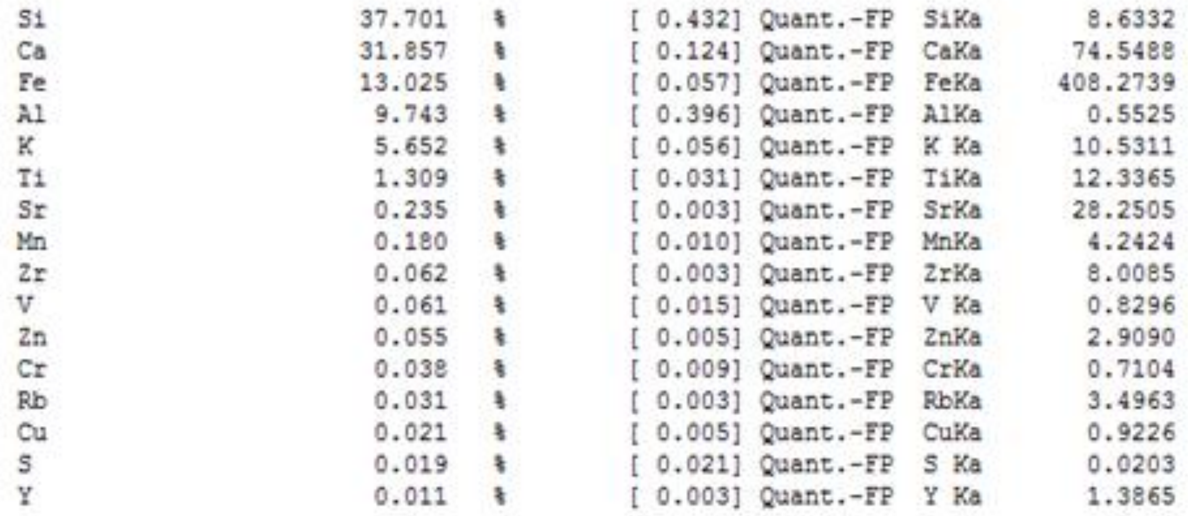
Po ' latni sikoniy with alloying them (up to 0.8 %) mechanical properties and again processing increases . From this except a little amount electric permeability when no mis and his solidification of hardening materials and heat endurance does .

Zirconium has the ability to burn at high speeds with almost no smoke with oxygen in the air. Slight ignition (250 ^{0} C). This creates the highest temperature for metal fuels (4550 ^{0} C). The four oxides of zirconium formed at high temperatures reflect a significant amount of light, which is widely used in pyrotechnics (in the manufacture of fountains in the musculoskeletal system). in the production of chemical sources of light used in various fields of human activity (verbs are used in photography as light rockets, light bombs as disposable flashing lamps.)

In the mining industry, along with Zirconium, Manganese steels can be widely used in the manufacture of balls for ball mills and in the manufacture of molds for stone crushing mills. The balloons currently used in the mining industry prevent collapse (30%).

Laboratory analysis of minerals in Uzbekistan in diagrams 1, 2, 3





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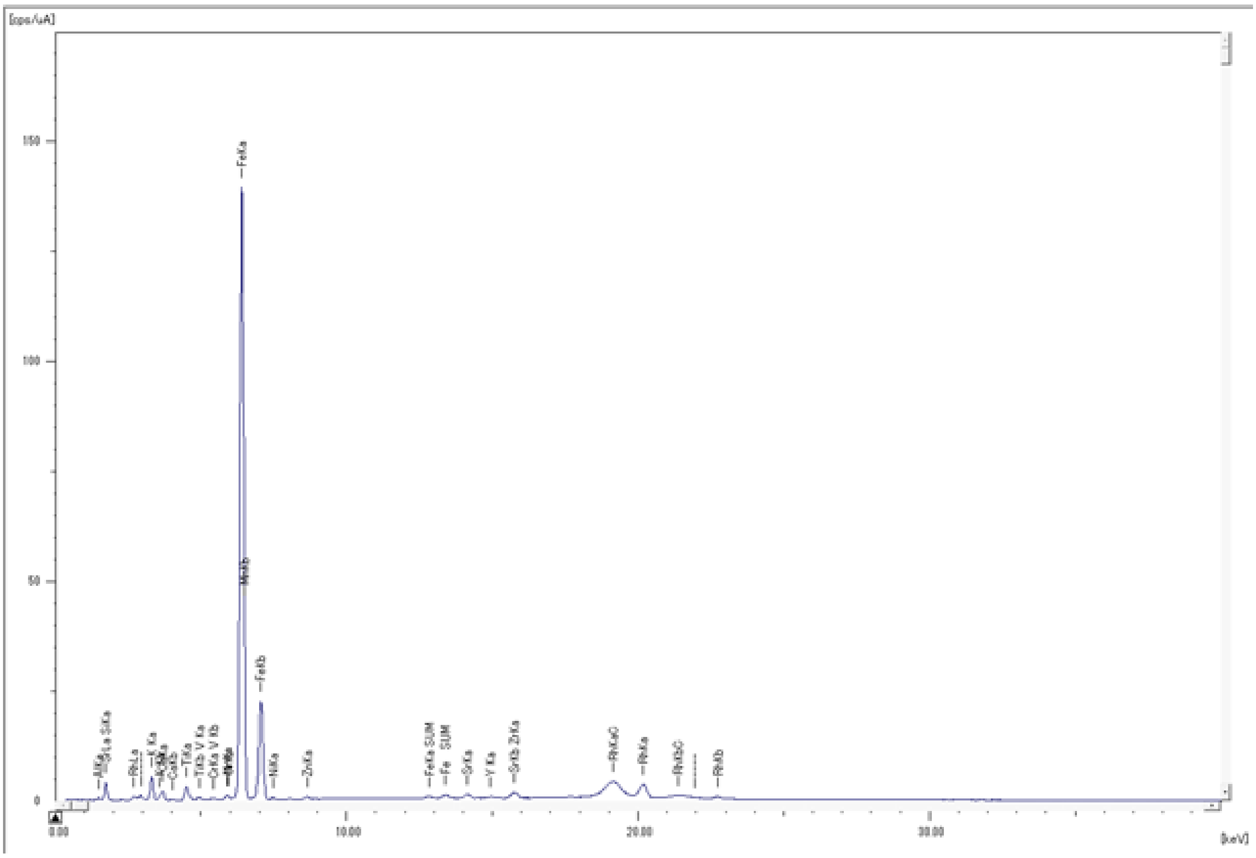
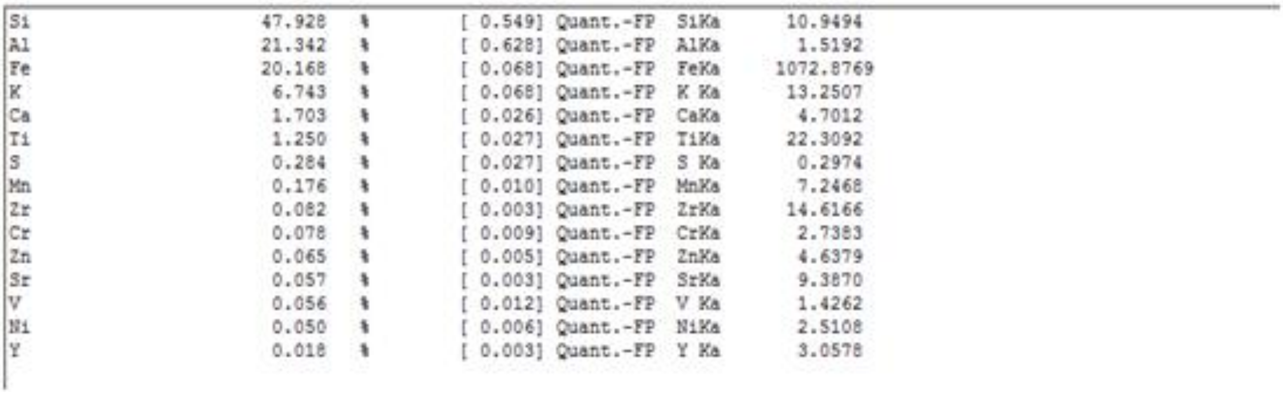
Si          37.701  %    [ 0.432] Quant.-FP  SiKa     8.6332
Ca          31.857  %    [ 0.124] Quant.-FP  CaKa    74.5488
Fe          13.025  %    [ 0.057] Quant.-FP  FeKa   408.2739
Al           9.743  %    [ 0.396] Quant.-FP  AlKa     0.5525
K            5.652  %    [ 0.056] Quant.-FP  K Ka    10.5311
Ti           1.309  %    [ 0.031] Quant.-FP  TiKa    12.3365
Sr           0.235  %    [ 0.003] Quant.-FP  SrKa    28.2505
Mn           0.180  %    [ 0.010] Quant.-FP  MnKa     4.2424
Zr           0.062  %    [ 0.003] Quant.-FP  ZrKa     8.0085
V            0.061  %    [ 0.015] Quant.-FP  V Ka     0.8296
Zn           0.055  %    [ 0.005] Quant.-FP  ZnKa     2.9090
Cr           0.038  %    [ 0.009] Quant.-FP  CrKa     0.7104
Rb           0.031  %    [ 0.003] Quant.-FP  RbKa     3.4963
Cu           0.021  %    [ 0.005] Quant.-FP  CuKa     0.9226
S            0.019  %    [ 0.021] Quant.-FP  S Ka     0.0203
Y            0.011  %    [ 0.003] Quant.-FP  Y Ka     1.3865
```

1-diagram

Namangan-19

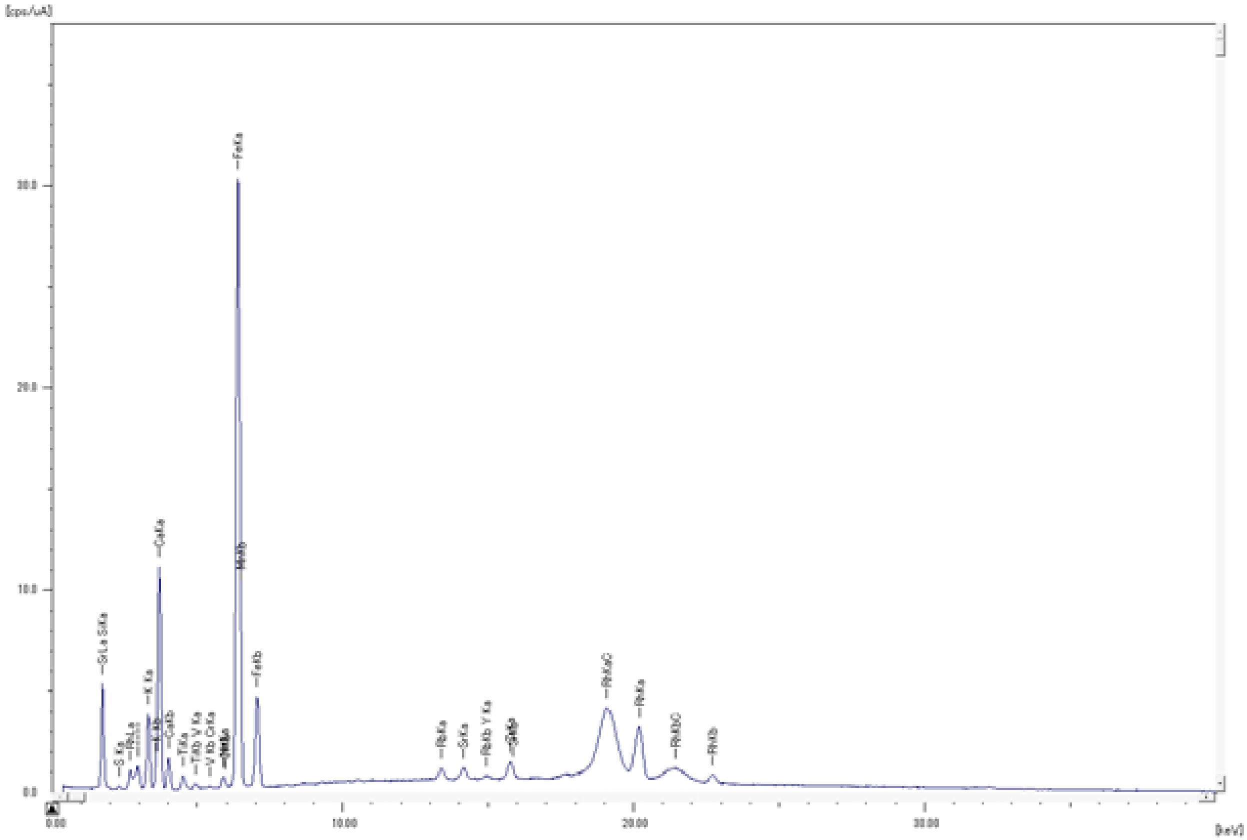


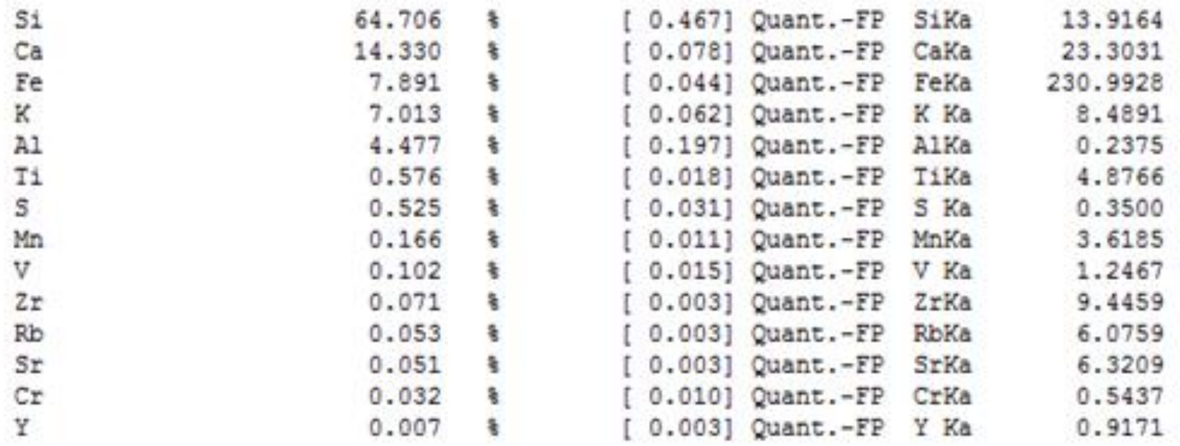


```
Si                  47.928   %       [ 0.549] Quant.-FP  SiKa     10.9494
Al                  21.342   %       [ 0.628] Quant.-FP  AlKa      1.5192
Fe                  20.168   %       [ 0.068] Quant.-FP  FeKa   1072.8769
K                    6.743   %       [ 0.068] Quant.-FP  K Ka     13.2507
Ca                   1.703   %       [ 0.026] Quant.-FP  CaKa      4.7012
Ti                   1.250   %       [ 0.027] Quant.-FP  TiKa     22.3092
S                    0.284   %       [ 0.027] Quant.-FP  S Ka      0.2974
Mn                   0.176   %       [ 0.010] Quant.-FP  MnKa      7.2468
Zr                   0.082   %       [ 0.003] Quant.-FP  ZrKa     14.6166
Cr                   0.078   %       [ 0.009] Quant.-FP  CrKa      2.7383
Zn                   0.065   %       [ 0.005] Quant.-FP  ZnKa      4.6379
Sr                   0.057   %       [ 0.003] Quant.-FP  SrKa      9.3870
V                    0.056   %       [ 0.012] Quant.-FP  V Ka      1.4262
Ni                   0.050   %       [ 0.006] Quant.-FP  NiKa      2.5108
Y                    0.018   %       [ 0.003] Quant.-FP  Y Ka      3.0578
```

2-diagram

Namangan-60





```
Si       64.706   %    [ 0.467] Quant.-FP  SiKa    13.9164
Ca       14.330   %    [ 0.078] Quant.-FP  CaKa    23.3031
Fe        7.891   %    [ 0.044] Quant.-FP  FeKa   230.9928
K         7.013   %    [ 0.062] Quant.-FP  K Ka     8.4891
Al        4.477   %    [ 0.197] Quant.-FP  AlKa     0.2375
Ti        0.576   %    [ 0.018] Quant.-FP  TiKa     4.8766
S         0.525   %    [ 0.031] Quant.-FP  S Ka     0.3500
Mn        0.166   %    [ 0.011] Quant.-FP  MnKa     3.6185
V         0.102   %    [ 0.015] Quant.-FP  V Ka     1.2467
Zr        0.071   %    [ 0.003] Quant.-FP  ZrKa     9.4459
Rb        0.053   %    [ 0.003] Quant.-FP  RbKa     6.0759
Sr        0.051   %    [ 0.003] Quant.-FP  SrKa     6.3209
Cr        0.032   %    [ 0.010] Quant.-FP  CrKa     0.5437
Y         0.007   %    [ 0.003] Quant.-FP  Y Ka     0.9171
```

3-diagram

Muruntauv-21

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