



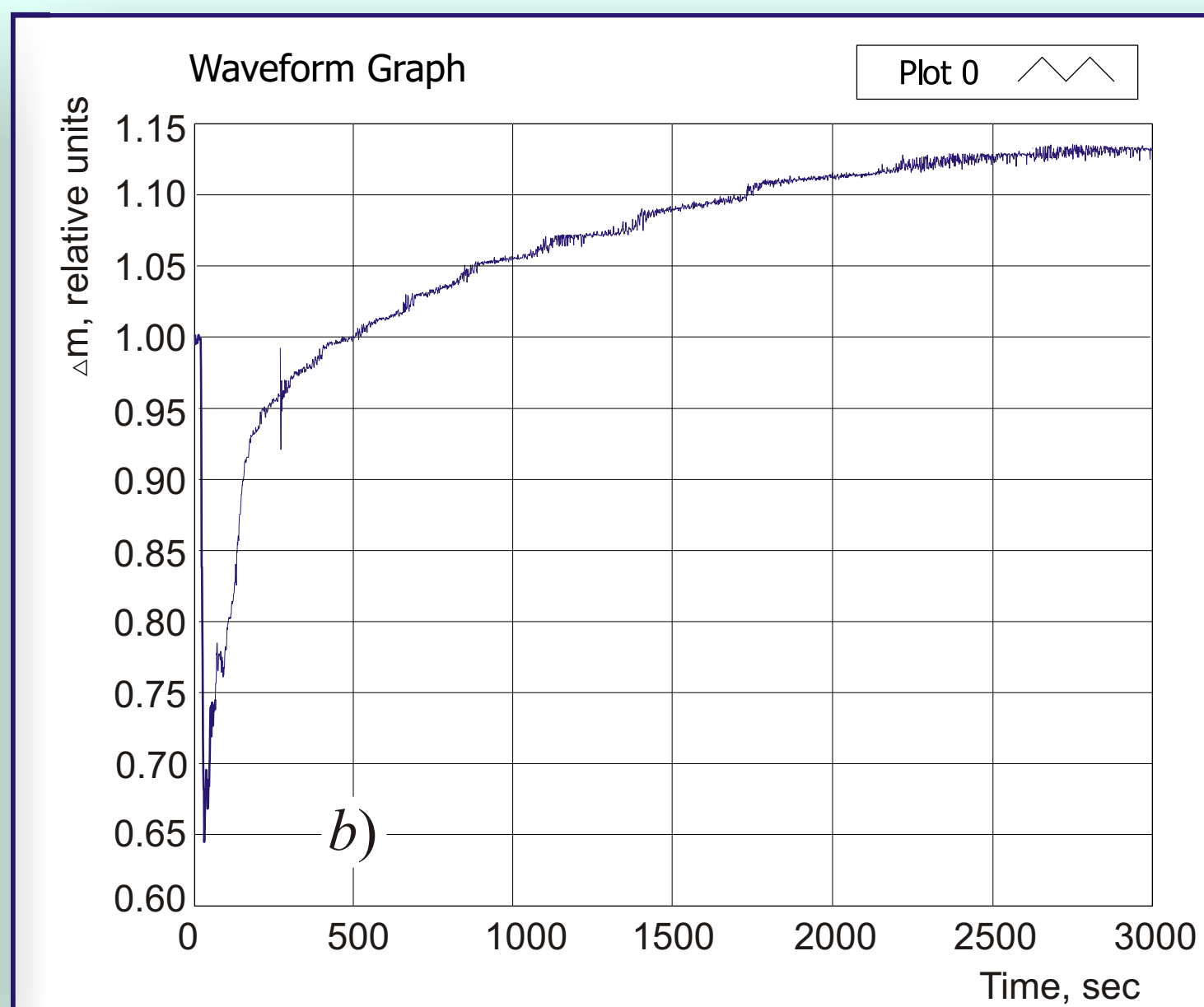
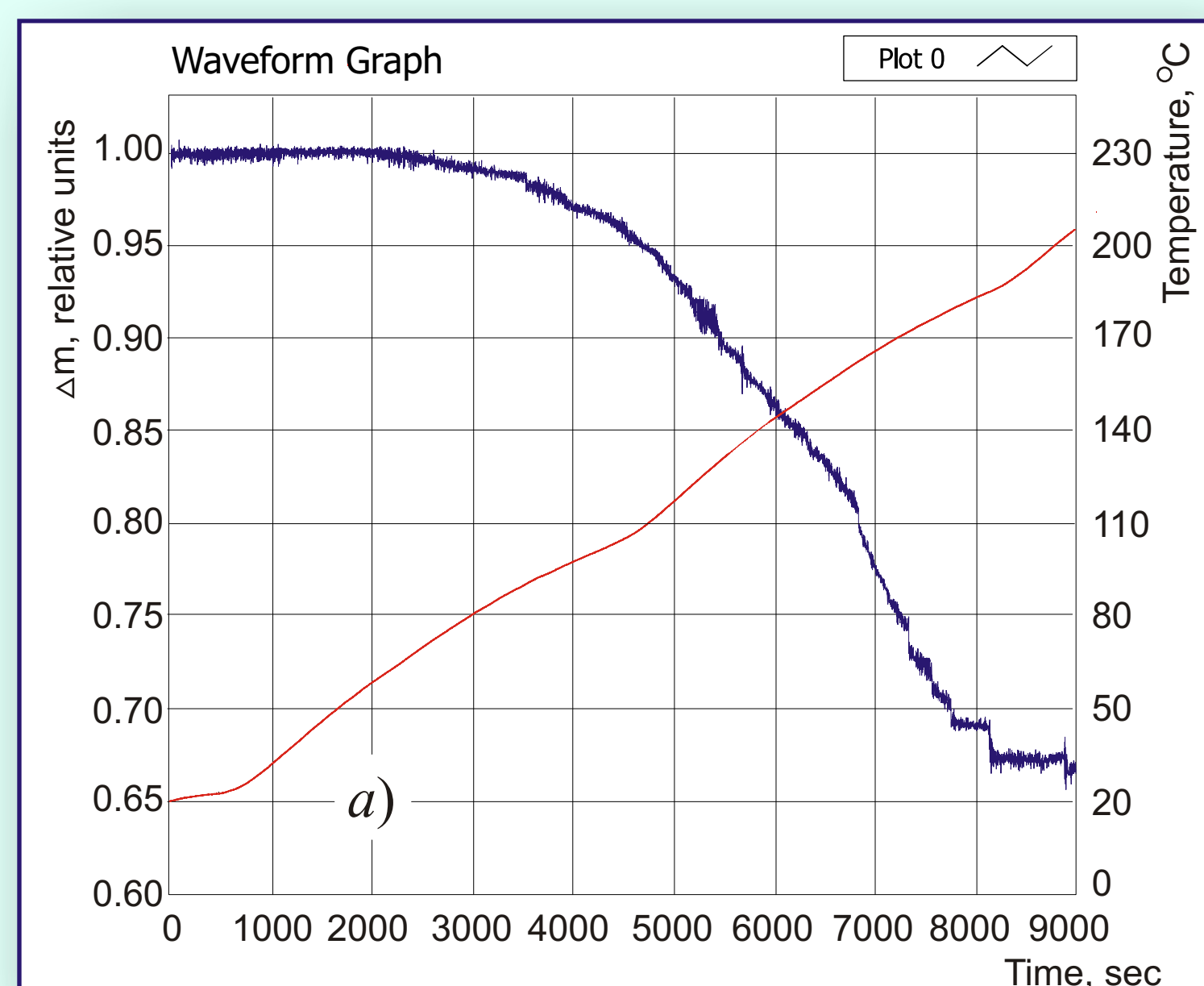
Before conducting research all surfaces of the experimental installation interacting with fluorine and reaction gaseous products were being passivated by the mixture of fluorine and argon, first under the room's temperature during 24 hours and then under 70 °C and then under 120 °C during 24 hours. And after that the nickel small vessel 14 was being hung on the thread into the reactor 13 with the sample KBr.

Further on the installation was vacuumed and checked for inleakage whose value did not exceed $2 \cdot 10^{-3}$ mm. Hg/hour. After the checking of installation's sealing there was conducted the heating of the reactor till the working temperature and the heating of sorption column 10 up to the 100 °C for the quantitative catching of the fluorine hydrogen from anode gas. The reactor is filled with fluorine with the dissolving by argon from tank 7 in designated ratios.

The temperature control in the reaction area was conducted remotely with the assistance of temperature detector 5 and the values were taken to the PC monitor depending on temperature (°C) to time (sec) ratio. The automatic adjusting of the reactor 13's heating temperature was conducted by detector OVEN TRM 1A, accuracy rate 0,25. The measuring of the mass of the sample 14 is conducted with the help of the detector 15 and is taken to the PC monitor depending on sample mass (grams) to time (sec) ration.

The end of the process of fluorination was determined according to the established, not changed value of the sample mass to time. The conduction of the fluorine and argon was finalized, the installation's evacuation is conducted, the remaining fluorine agent and the reaction products were caught on sorbent in tank 18. The installation was being disassembled, the nickel small vessel was recovered and the product received was subject to control weighting and to be analyzed by standard titrometric methods.

On the **picture 2** there are represented the dependency curves of the changing of the sample mass according to time, which are given in the temperature interval from 20 to 207 °C (**picture 2a**) as well as under the constant temperature of 60 °C (**picture 2b**).



Picture. 2. Dependence of sample mass changing at time in a process of fluorination
a) — - mass changing of $KBrF_4$ in fluorine in dependence at time in temperature interval at 20 to 207 °C
 — - temperature changing in reaction zone in dependence at time;
b) sample mass changing in dependence at time at constant temperature 60 °C

On the **picture 2a** there are described the analysis of the thermal stability of potassium tetrafluorobromate in the fluorine medium. As seen from the data of the **picture 2a** in temperature interval up to 60 °C the $KBrF_4$ is rather stable. Under the higher temperatures the potassium tetrafluorobromate in fluorine medium begins to dissipate, of which the reducing of the sample mass witnesses. The probable explanation of this phenomena can be named as the further fluorination of the potassium tetrafluorobromate up to potassium hexafluorobromate ($KF \cdot BrF_3$) which is an unstable compound in current conditions. [3].

For further analysis (**picture 2b**) there was chosen the temperature of 60 °C as maximal temperature under which the $KBrF_4$ the desired product is a stable compound in the fluorine environment. The research was conducted according to the methods described hereabove. As seen from the **picture 2b** the process takes place in two stages; the **first stage** is described by the losing mass the **second one** by its increase. Going from the results obtained by the authors the following mechanism of the going of the process of fluorination is supposed



At the **first stage** the fluorine as the more active element displaces the bromium from the compound with potassium (reaction 7) thus the potassium fluorine and gaseous bromine which is present in the view of vapors in the pores of fine dispersed KF. The interaction of the bromine with fluorine can lead to the creation of three different bromine fluorides (reaction 8, 9, 10). Nevertheless judging by the data represented in [3] under the temperature of 60 °C there is most probable the going of the reaction 9. Thus the obtained brominotrifluoride interacts with the created potassium fluoride (reaction 11) which leads to the increasing of the sample mass (**second stage** of the **picture 2b**).

As per the results of the analysis one can make a conclusion about the completeness of the going fluorination process. As seen from the **picture 2b** the value of the conversion on the first stage was 69.2 %, the second stage ended practically in full with the value of conversion of 99.5% . And the value of the conversion of the summarized reaction was 69 %. Thus the product obtained is the compound of potassium tetrafluorobromide and unreacted potassium bromide. This is confirmed by the titrometric research.

In the work [15] the authors published they results of the method of obtaining of $KBrF_4$ by the method of interaction of liquid trifluorobromine with potassium fluorine. As seen from the comparison of these data one can point out that the $KBrF_4$, obtained according to the methods, described in [15] is the product of higher quality (with the contents of the target product of more than 90 %). But from the point of view of the industrial realization technology obtaining of $KBrF_4$ the method of simple fluorination looks more prospective as in this case there is no necessity to obtain, store and conduct work with the bromine trifluorine.

As the further working out of the technology of obtaining $KBrF_4$ by the method of the simple fluorination it is planned the creation of the lab prototype of the industrial screw reactor with horizontal location and the working out of the technological modes with the purpose of improving the target product quality.

Literature

- Mitkin V.N., Shavinsky B.M., Kamelin A.I.: The extraction of rare earths impurities from uranium dioxide by bromine trifluoride for their concentration and analytical detection. // Journal of analytical chemistry. 2000. T. 55. № 3. p. 286-288.
- Mitkin V.N., Fluoroxidants in analytical chemistry of noble metals. // Journal of analytical chemistry 2001. T. 56, N.2. - p.118-142.
- Nikolaev N.S., Suhoverhov V.F. and others. Chemistry of fluorine halogen compounds. M.: Science, 1965.
- Reprocessing of nuclear fuel by the method of fluorides volatility. M. Atomizdat, 1971. T.11V. p.1628.
- Scherbakov V.I., Zuev V.A., Parfenov A.V. Kinetics and fluorination mechanism of uranium, plutonium and neptunium compounds by fluorine and halogen fluorides. M.: Energoatomizdat, 1985.
- Nikolaev N.S., Suhoverhov V.F. and others. Chemistry of fluorine halogen compounds. M.: Science, 1965.
- Kiselev N.I., Lapshin O.N., Sadikova A.T., Suhoverhov V.F., Churbanov M.F. Production of dry sodium and barium fluorides by the thermal decomposition of their compounds with bromine trifluoride.// High-clean substances. 1987. № 3. p.178-182.
- Popov A.I., Kiselev U.M., Suhoverhov V.F., Chumaevsky N.A., Krasnyanskaya O.A., Sadikova A.T.: Research of thermal stability of alkaline tetrafluorobromates (III). // Journal of scientific chemistry.-1987. T.32. № 5. p. 1007-1012.
- Zherin I.I., Amelina G.N., and others. Volumetric IF5 and BrF3 properties. Report 2. Pressure of saturated bromine trifluoride vapor // Proceedings of Tomsk Polytechnic University. Tomsk, 2002. T. 305. Issue 3. p. 263273.
- Mitkin V.N. Physical-Chemical basis of the fluoroxidant's application in the noble metal's analytical chemistry (The Review) // Spectrochimica Acta, Part B, 2001, vol. 56/2, No 1, pp. 135-175.
- Mitkin V.N., Bir V.A., Logvinenko V.A. Chemical transformations of potassium tetrafluorobromate (III) under heating (thermoanalytical study in a carbon crucible) // Abstracts of 11th European Symposium on Fluorine Chemistry, Bled, Slovenia, September 17-22, 1995, p. 168.
- Cady G.H. Freezing point and vapor pressures of the system potassium fluoride hydrogen fluoride // J. Am. Chem.Soc., 1934, V. 56, No. 7, pp. 1431-1434.
- Rudnikov A.I., Zherin I.I., Gordienko V.V. and ath. / Thermal decomposition of BrF3 and NaF compounds // Proc. of the TPU.- 2002. - V 305, Is. 3.- P. 210-219.
- Mitkin V.N., Tsimbalist V.G., Zayakina S.B., Galizky A.A. // Application of potassium tetrafluorobromate(III) for the rapid decomposition and determination of noble metals in chromites and related materials // Spectrochimica Acta, 2003, vol. 58B, pp.297-310.
- Ostvald R.V., Shagalov V.V., Zherin I.I. and oth. Complex Compounds of Bromine Trifluoride and Alkaline Fluorides // Procc III Intern. workshop. ISIF 2008. ISBN 978-5-901888-68-1