National Research
Tomsk Polytechnic University

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Investigation of the $KFBr_4$ synthesis technique by fluorination of potassium bromide

Purpose of the Research

To evaluate the feasibility of the $KFBr_4$ synthesis by means of fluorination by elementary fluorine, compare this method to the liquid phase fluorination technique and investigate the applicability of this synthesis technique for industrial aims.

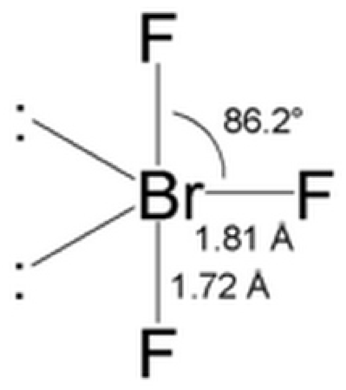
Application

$KFBr_4$ is a complex compound of BrF_3 with KF, which was recently proposed for the use as alternative to BrF_3. At room temperature $KFBr_4$ is a stable powder and has much lower chemical and corrosive activity therefore it is much more convenient for the work and storage and is much safer to handle compared to liquid BrF_3 [1, 2].

Due to it high oxidizing capacity BrF3 can fully oxidize noble metals.

The noble metals could be divided into two groups on the relative kinetic propensity to oxidation of BrF_3 [3].

- Fast-soluble metals Ag, Au, Ru, Ir, Os.
- Slow-soluble metals Pt, Pd, Rh.



Metals of the first group interact in a complex multistage mechanism through the formation of coordinating fluorides. In general there are following reaction schemes [3]:

$$6\,Ag + 8\,BrF_3 \rightarrow 6\,Ag[BrF_4] + Br_2, \quad (1)$$

$$2\,Au + 4\,BrF_3 \rightarrow 2\,[BrF_2^+][AuF_4^-] + Br_2, \quad (2)$$

$$6\,Me + 16\,BrF_3 \rightarrow 6\,[BrF_2^+][MeF_6^-] + 5\,Br_2, \quad (3)$$

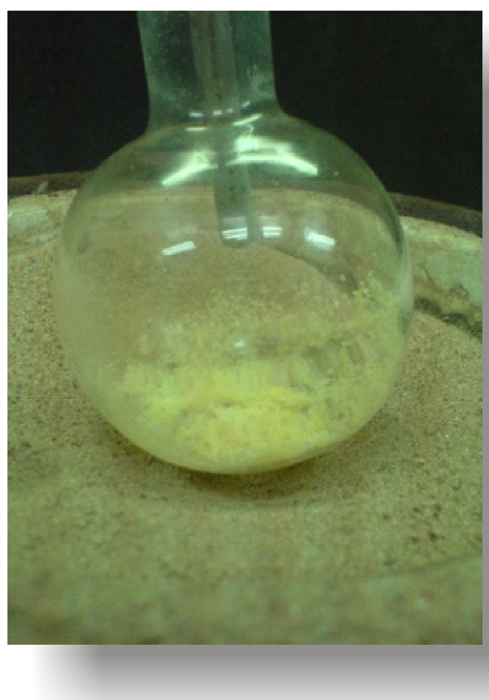
where Me Ru, Os, Ir.

Methods of $KBrF_4$ Synthesis

Two methods of $KBrF_4$ synthesis are researched in TPU [4]

liquid-phase fluorination, by the interaction between potassium fluoride and liquid bromine trifluoride,

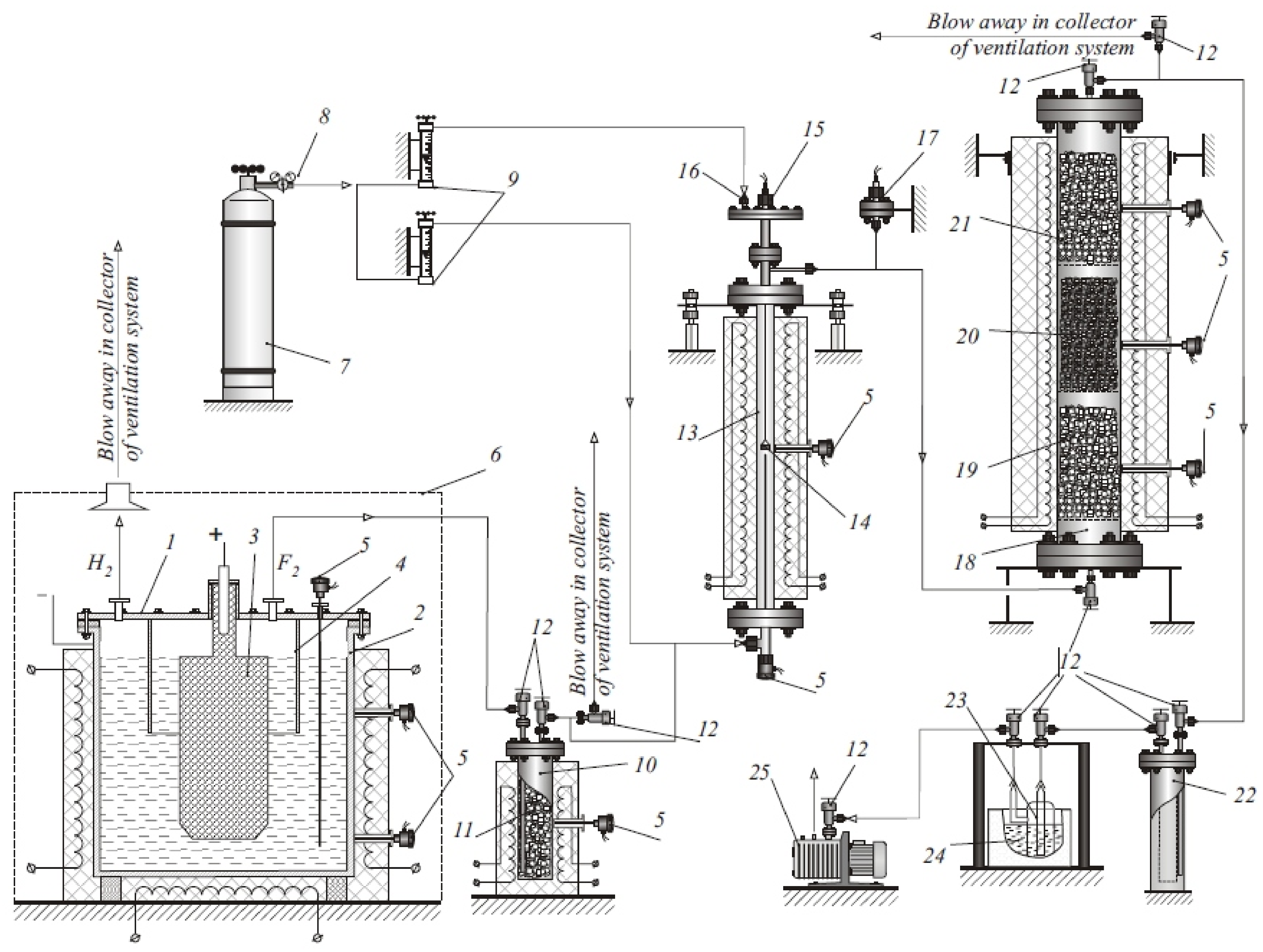
$$KF + BrF_3 \rightarrow KBrF_4 \quad (4)$$



gaseouse fluorination of potassium bromide with elementary fluorine

$$KBr + F_2 \rightarrow KBrF_4 \quad (5)$$

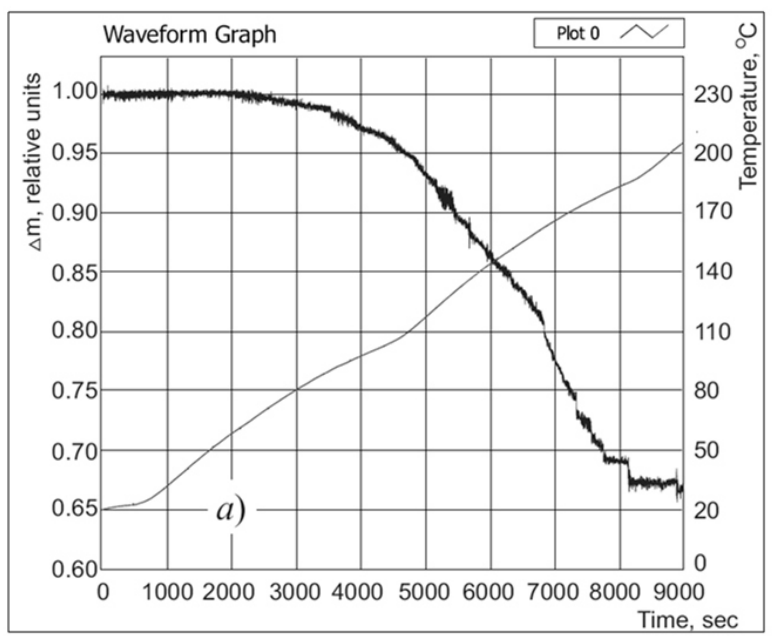
Kinetic Research of Potassium Bromide Fluorination process



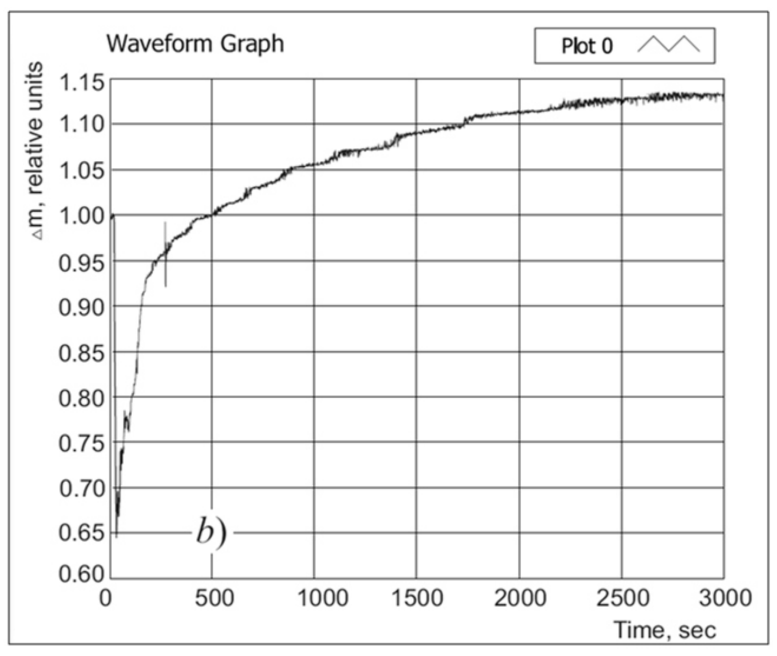
Scheme of the experimental installation

Potassium bromate before fluorination

Products after fluorination



Time Dependence of the Temperature and Mass of $KBrF_4$



Time Dependence of Mass KBr at Fluoridation. The Temperature is 60 °C

$$2KBr + F_2 \rightarrow 2KF + Br_2, \quad (5)$$

$$Br_2 + F_2 \rightarrow 2BrF, \quad (6)$$

$$Br_2 + 3F_2 \rightarrow 2BrF_3, \quad (7)$$

$$Br_2 + 5F_2 \rightarrow 2\,BrF_5, \quad (8)$$

$$KF + BrF_3 \rightarrow KBrF_4, \quad (9)$$

Qualitative Reaction of $KBrF_4$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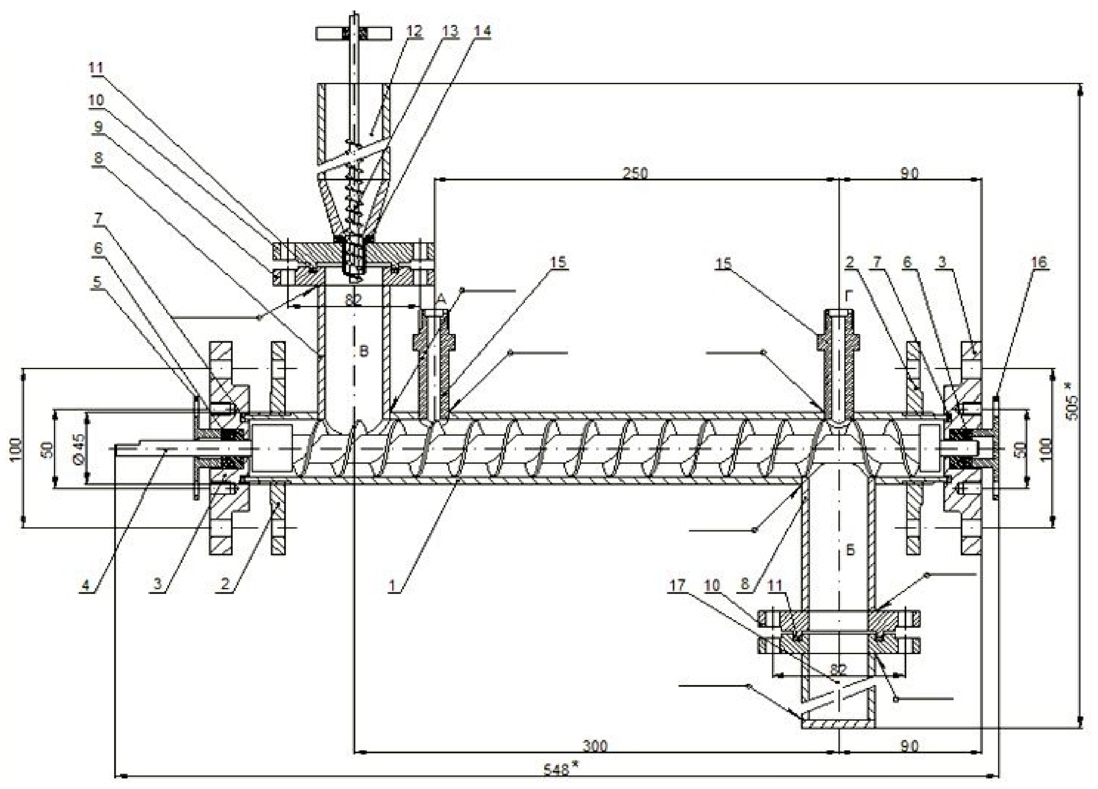
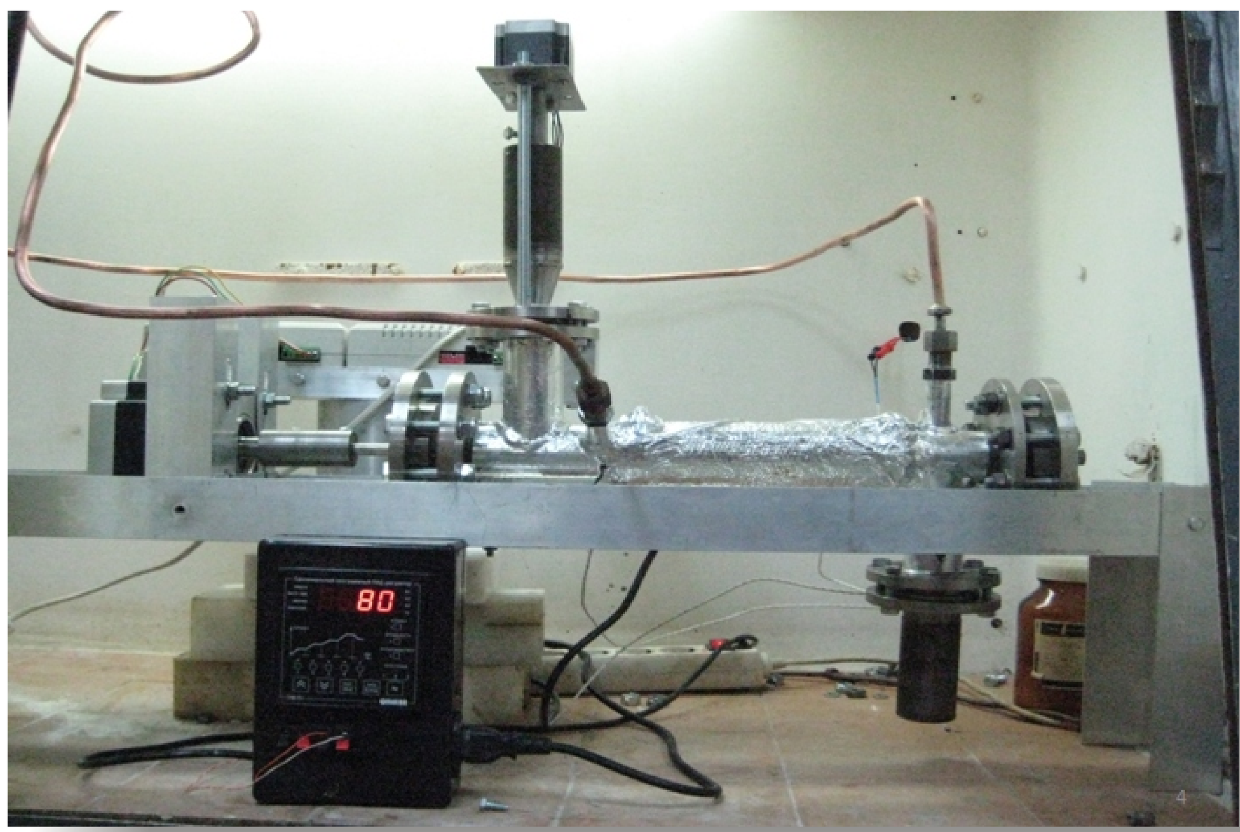
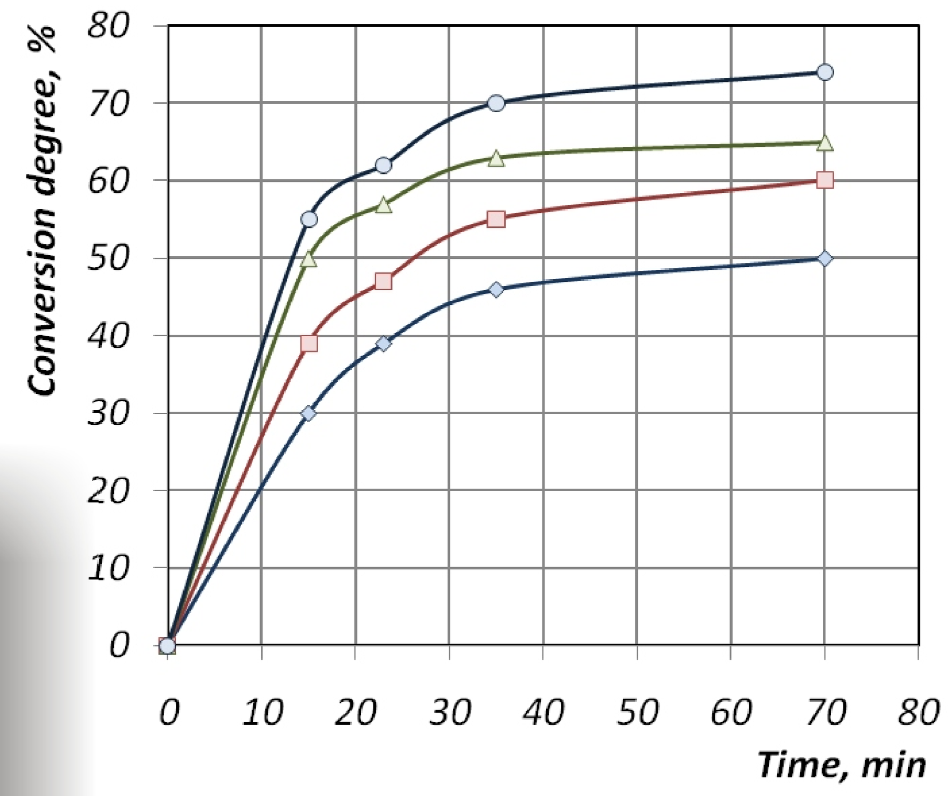
Testing of the Industrial Pilot Reactor



Assemble drawing, of the horizontal reactor for the fluorination of potassium bromide

Horizontal reactor for fluorination of the potassium bromide



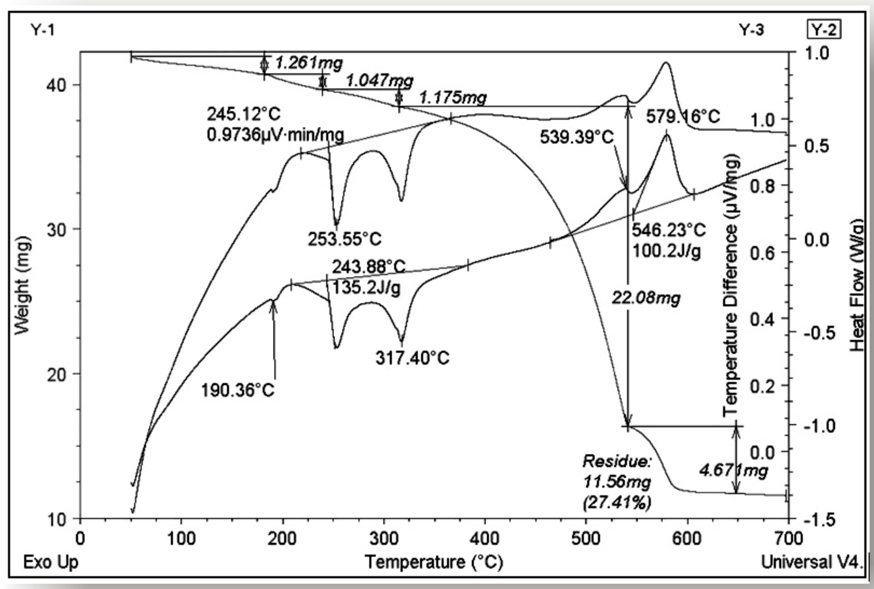


Dependance of the conversion degree from time at difference temperatures

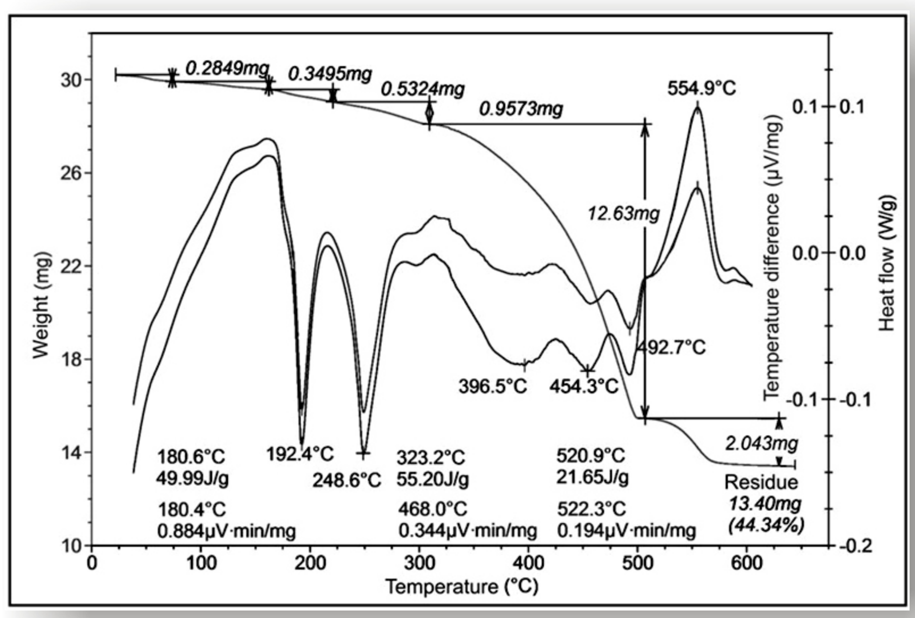
- 140 Celsius Degree
- 120 Celsius Degree
- 100 Celsius Degree
- 80 Celsius Degree

Comparison of the two samples synthesized by two different methods

Thermal analytical data of $KBrF_4$ samples which synthesized of two different methods



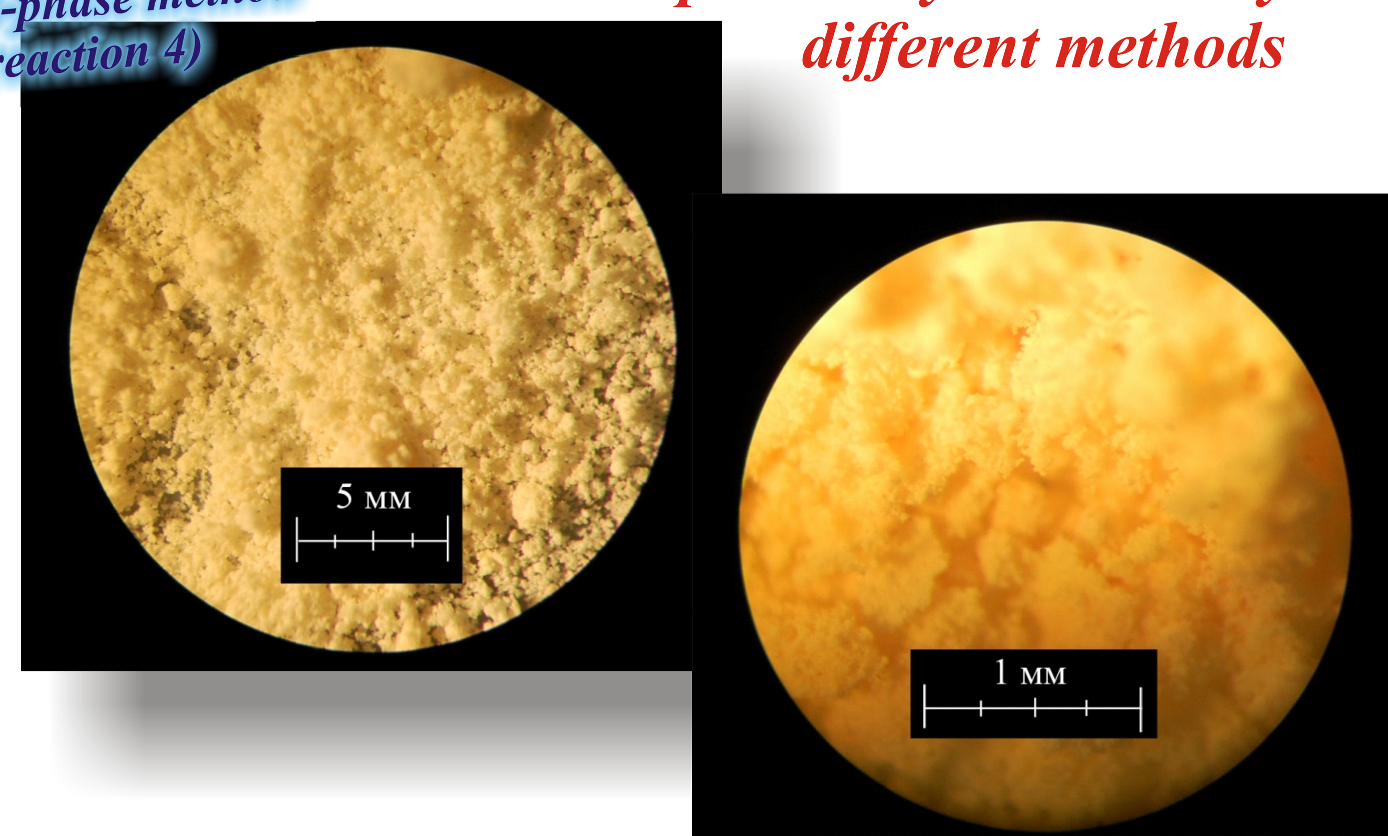
Liquid-phase method (reaction 4)



Gaseous-phase method (reaction 5)

Micro-photos of the $KBrF_4$ powder synthesized by two different methods

Liquid-phase method (reaction 4)



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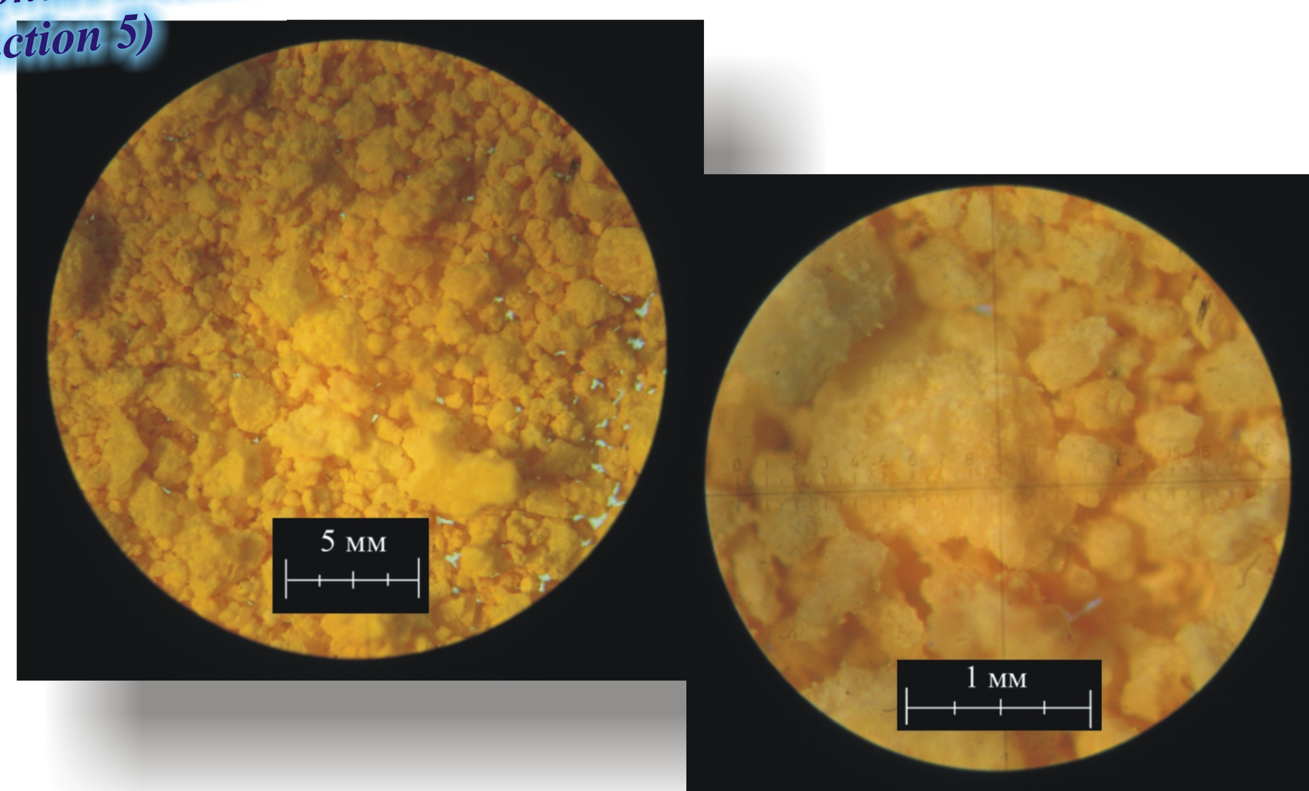

Conclusion

New methods for the synthesis of the fluorinating material is present. The Possibility of $KBrF_4$ production in industrial plants is demonstrate.

Literature

[1] V. Mitkin. Fluorination-oxidizing agents in the Nobel metals analysis. In *Journal of Analytical Chemistry*, pages 118-142, Vol. 56, #2, 2001.
[2] V. Mitkin. Fluorination of Iridium Metal and its Application Possibilities in the Synthesis, Analysis and Recovery Technology for Secondary Raw Materials (Review), Iridium. In *Proceedings of International Symposium TMS-2000*, pages 377-390, Nashville, Tennessee, March 2000.
[3] V. Mitkin, S. Zayakina, V. Tsimbalist. Sample preparation with using oxidative-fluorinative decomposition and sulphatisation in case of Nobel metals determination in standard geological samples. In *Journal of Analytical Chemistry*, pages 22-33, Vol. 58, #1, 2003.
[4] R. Ostvald, V. Shagalov, and others. Complex compounds of brome(III)fluoride with fluorides of alkali metals. In *Proceedings of II International workshop ISIF 2008*, pages 92-97, Russia, Vladivostok, September 2008, ISBN 978-5-901888-68-1.