Scientific article
UDC 546.74+544.35
DOI: 10.52957/2782-1900-2025-6-1-112-118

PRODUCTION OF HIGH-PURITY TETRAKIS(TRIFLUOROPHOSPHINE)NICKEL

D.M. Zimina[1], O.Yu. Troshin[1,2], A.Yu. Sozin[1,2], P.A. Otopkova[2], A.M. Potapov[2]

Darya Mikhailovna Zimina, Postgraduate Student; **Oleg Yuryevich Troshin,** Candidate of Chemical Sciences, Associate Professor; **Andrey Yuryevich Sozin,** Doctor of Chemical Sciences; **Polina Andreyevna Otopkova,** Candidate of Chemical Sciences; **Alexander Mikhailovich Potapov,** Candidate of Chemical Sciences.

[1]National Research Lobachevsky State University of Nizhni Novgorod, 603022, Russia, Nizhny Novgorod, 23, Gagarin prospekt; *daria.m.zimina@yandex.ru*

[2]G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (ICHPS RAS), 603950, Russia, Nizhny Novgorod, 49, Tropinina str.

Keywords: *tetrakis(trifluorophosphine) of nickel, impurity, distillation, deep purification, partition coefficient.*

Abstract. *The paper presents the results of obtaining samples of high-purity tetrakis(trifluorophosphine) nickel. Chromatography-mass spectrometry and inductively coupled plasma mass spectrometry indicate impurity, elemental, and molecular composition of the initial and purified samples. If a distillation rate of 80 µl/min and an extraction fraction of 50%, the content of iron, copper, and cobalt limiting impurities is below 0.01 ppm;* PF_3, CH_2Cl_2 *and hydrocarbons are at the level of* $n\text{-}10^{-3} \div n\text{-}10^{-5}$ *mol%.*

For citation:
Zimina D.M., Troshin O.Yu., Sozin A.Yu., Otopkova P.A., Potapov A.M. Production of high-purity tetrakis(trifluorophosphine)nickel // *From Chemistry Towards Technology Step-by-Step*. 2025. Vol. 6, Iss. 1. P. 112-118. URL: https://chemintech.ru/ru/nauka/issue/5879/view

Introduction

Nickel consists of five stable isotopes ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, ^{64}Ni; there are also known radioactive isotopes of ^{59}Ni ($\tau_{1/2}$ 10^5 years), ^{63}Ni (10^2 years) and ^{56}Ni (6,08 days) [1, 2]. Nickel isotopes are used as starting material in the synthesis of various nuclides: ^{61}Ni и ^{64}Ni for the synthesis of ^{61}Cu and ^{64}Cu [2-4]; ^{60}Ni for the synthesis of ^{57}Co [5]; ^{62}Ni for the synthesis of radioactive isotope ^{63}Ni for compact power supplies of microwatt power with a long lifetime [5, 6]. Individual nickel isotopes may also be of fundamental interest for studying isotopic effects in structural materials [2, 7].

Tetrakis(trifluorophosphine) nickel $Ni(PF_3)_4$ is used as a working substance for the production of nickel isotopes by ultracentrifugation due to high vapour pressure, relative chemical and thermal stability, and monoisotopicity of fluorine and phosphorus [6, 8-10].

For these applications $Ni(PF_3)_4$ of high purity is required. However, there is no information on the impurity composition of $Ni(PF_3)_4$, methods of its purification and obtaining of high-purity substance in the scientific literature. Indeed, there is one published paper on the

---

qualitative impurity composition of the vapour phase of the $Ni(PF_3)_4$ sample obtained by the reaction of nickel with phosphorus (III) fluoride [11]. Hydrocarbons, phosphorus halides, and mixed alkyl-fluorophosphine derivatives of nickel are the main molecular impurities in $Ni(PF_3)_4$. However, the quantitative content of these impurities is not presented in [11], nor is the impurity elemental composition of the substance investigated. Hence, the study of the impurity composition, obtaining and characterisation of high-purity $Ni(PF_3)_4$ samples is an urgent task.

Impurities in $Ni(PF_3)_4$ can be divided into four groups. Each group requires individual approaches for investigation and isolation.

The first group includes impurities of chemical elements – similar metals and non-metals with high affinity to nickel. In [11] by inductively coupled plasma mass spectrometry (ICP-MS) analysis of a nickel sample the following chemical elements (mg/kg) make the largest impurity contribution: Fe (236 ± 8), P (до 58 ± 6), Cu (16.0 ± 2.0), As (29.0 ± 2.0), Ag (11.1 ± 0.3), Sb (11.0 ± 1.0), Bi (10.9 ± 0.3), Co (7.0 ± 2.0) [12]. The limiting impurities in nickel isotopes are copper, iron, and cobalt [13]. Their isotopes enter into parallel radioconversions and contaminate the obtained target nuclides.

The reaction of $Ni(PF_3)_4$ production is performed in excess of phosphorus trifluoride. It is the main polluting precursor and refers to the second group of impurities. Phosphorus trifluoride has a saturated vapour pressure of more than $1{\cdot}10^4$ mmHg. It negatively affects the ultracentrifugation process [7]; the PF_3 impurity is limiting for $Ni(PF_3)_4$. Distillation and gas separation methods on a cascade of centrifuges are used for purification of $Ni(PF_3)_4$ of phosphorus trifluoride [7].

The third group of impurities includes limiting and aromatic hydrocarbons; their derivatives and halogen hydrocarbons. Their presence is determined by the content of these impurities in the initial substances. Their content varies at $n{\cdot}10^{-3}$ – $n{\cdot}10^{-4}$ wt.%. These impurities can react with nickel, displacing PF_3 and forming complexes such as $Ni(PF_3)_3(PF_2OR)$ and $Ni(PF_3)_3(PF_2R)$ (R is a hydrocarbon radical) [11]. Reducing the amount of these impurities will decrease the probability of obtaining mixed fluorophosphine-hydrocarbon complexes. Their presence negatively affects the ultracentrifugation process.

The fourth group consists of impurities of common (constant) gases (O_2, N_2, Ar, etc.). Their presence increases the total pressure of the mixture and reduces the efficiency of isotopic separation.

Therefore, the physicochemical properties of the base and the considered impurities assume the distillation method is promising for the purification of $Ni(PF_3)_4$. The purpose of this study is to determine the equilibrium liquid-vapour partition coefficients for $Ni(PF_3)_4$ - impurity systems and to obtain samples of high-purity $Ni(PF_3)_4$ by distillation method.

Main body

We used $Ni(PF_3)_4$ obtained by the reaction of nickel and phosphorus trifluoride according to the procedure proposed in [14] for distillation purification experiments. To obtain a high purity sample, we loaded the $Ni(PF_3)_4$ under study into a 150 cm^3 molybdenum glass ampoule and distilled at 298 K with an evaporation rate of 8.0 ± 0.2 μL/min with the target middle fraction taken. We examined the obtained samples by chromatography-mass spectrometry using an Agilent 6890/MSD 5973N. We performed sample introduction using a vacuum-operated pipetting system. We dosed the sample into the chromatography column using a Valco EH2C6WEZPH-CER5 automatic two-position dosing tap.

We determined the content of molecular impurities in the initial sample and the sample obtained after distillation purification by chromatography-mass spectrometry. The results are presented in Table 1. The table shows varying of the impurity concentration in the range of $n \cdot 10^{-3}$ to $n \cdot 10^{-1}$ mol%, with a significant decrease in impurity concentration.

Table 1. Molecular impurity content in the initial and purified samples of $Ni(PF3)_4$ and obtained liquid-vapour partition coefficients for the systems $Ni(PF_3)_4$ - impurity

Impurity	Content in the initial sample $Ni(PF_3)_4$, mol.%	Content in the obtained sample $Ni(PF_3)_4$, mol.%	α
PF_3	0.632	$3.2 \cdot 10^{-3}$	26.3
$n\text{–}C_5H_{12}$	0.149	$6.5 \cdot 10^{-4}$	3.6
CH_2Cl_2	0.601	$1.1 \cdot 10^{-4}$	3.1
$i\text{–}C_5H_{12}$	0.015	$1.8 \cdot 10^{-4}$	1.2
3-ethylhexane	0.003	$3.1 \cdot 10^{-5}$	2.0
3-methylhexane	0.002	$5.0 \cdot 10^{-5}$	2.0
$Ni(PF_3)_3(PF_2OC_2H_5)$	0.147	$1.1 \cdot 10^{-3}$	3.7
$n\text{–}C_7H_{16}$	0.007	$9.7 \cdot 10^{-5}$	1.8
2,2-dimethylhexane	0.009	$7.7 \cdot 10^{-4}$	2.0

The total mole fraction of the above impurities in the obtained sample does not exceed $5 \cdot 10^{-3}$%; the mass fraction $Ni(PF_3)_4$ is more than 99.998%.

We determined the impurity content of chemical elements by inductively coupled plasma mass spectrometry using an ELEMENT 2 single-collector high-resolution inductively coupled plasma mass spectrometer [15]. The results are presented in Table 2. The impurity concentration varied in the range of $n \cdot 10^{-5}$ – $n \cdot 10^{1}$ ppmw.

Table 2. Impurity content of chemical elements in the initial and purified samples $Ni(PF_3)_4$

Impurity	Initial content, ppmw	Content in the obtained sample, ppmw	Impurity	Initial content, ppmw	Content in the obtained sample, ppmw
Al	0.6	0.1	Mo	0.01	<0.004
As	0.03	0.001	Na	2	<1
B	0.5	<0.05	Nb	0.005	<0.001
Ba	0.03	<0.02	Pb	0.002	<0.001
Bi	0.002	<0.00003	Sb	0.001	<0.001
Cd	0.004	<0.001	Si	20	0.3
Cd	0.05	0.002	Sr	0.05	0.003
Co	0.01	0.005	Ta	0.006	0.002
Cr	0.005	<0.001	Te	0.04	0.002
Cu	0.06	<0.01	Ti	0.1	0.005
Fe	0.1	<0.01	Tl	0.0005	<0.0003
Ga	0.05	0.002	U	0.00002	<0.00003
In	0.003	<0.001	V	0.1	<0.005
Lu	0.003	<0.002	W	0.003	<0.002
Mg	0.2	<0.03	Zn	0.05	0.01
Mn	0.002	<0.001	–	–	–

According to the data from Table 2, there is a significant reduction in the content of all impurities of chemical elements, including the limiting impurities of iron and copper.

We performed experiments to determine the values of the effective liquid-vapour partition coefficient in the system $Ni(PF_3)_4$ - impurities by the method of Rayleigh distillation on the unit; the scheme is given in [16]. The main units of the apparatus are a glass ampoule with a model mixture and a magnetic stirrer placed in a thermostat and a receiving cylinder cooled with liquid nitrogen. We regulated the evaporation rate of the model mixture by fine adjustment valve and monitored by the exemplary vacuum gauge BO 11201. We conducted experiments at a temperature of 298 K, the duration of experiments was 5-300 min. We determined the composition of the mixtures by chromatography-mass spectrometry.

We calculated the values of effective liquid-vapour partition coefficients α for $Ni(PF_3)_4$ - impurity systems using the Rayleigh formula [16, 17]:

$$\frac{x}{x_0} = \left(\frac{V}{V_0}\right)^{\alpha-1},$$

where V_o, x_o, V, x is the liquid volume and impurity concentration in the distillation flask before distillation and after distillation, respectively.

Fig. 1 shows the dependence of the effective partition coefficient on the inverse evaporation rate for a number of impurities in $Ni(PF_3)_4$. The value of equilibrium α was found by extrapolating the dependence of the effective partition coefficient of the inverse of the evaporation rate to the zero evaporation rate.

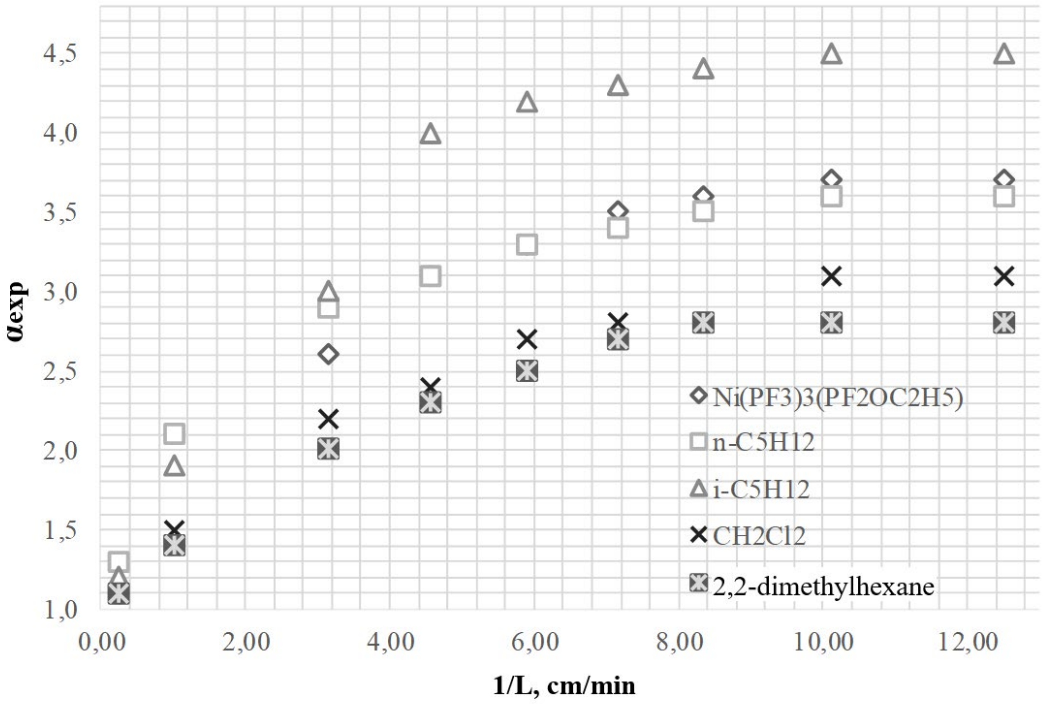

Fig. 1. Dependence of the effective vapour-liquid partition coefficient in the $Ni(PF_3)_4$ - impurities system on the inverse evaporation rate 1/*L*

To obtain samples of high-purity $Ni(PF_3)_4$, we applied multiple distillation of the initial mixture with selection of portions of distillate and cube residue [16, p. 58]. During distillation, we investigated the distribution of impurities of pentane and $Ni(PF_3)_3(PF_3OR)$ as a function of the fraction sampled. We poured 100 mL of initial $Ni(PF_3)_4$ into a glass ampoule and distilled it at 298 K into a liquid nitrogen-cooled receiving ampoule. We removed the receiving ampoule after taking about 10 cm^3 of liquid and replaced it with the next ampoule. Ten samples of $Ni(PF_3)_4$ as a two-phase system and a solid non-volatile powdery residue were obtained. We determined the composition of liquid and vapour phases of the samples by chromatography-mass spectrometry.

According to the results of the study, we constructed impurity distribution curves depending on the fraction of the sampled substance as it shown in Fig. 2.

The figure shows that the optimal scheme of the process is the selection of 20 - 30% of fractions enriched with more volatile impurities, separation of 30 - 40% of the target middle fractions, and further rejection of cube fractions.

We dissolved the solid residue in dilute 'CP' grade nitric acid and dried the obtained solution on tantalum substrate at 300 °C. Then we determined the elemental composition by laser mass spectrometry (LMS) on an EMAL-2 mass spectrometer according to the procedure given in [18]. Table 3 presents the elemental composition of the solid residue.

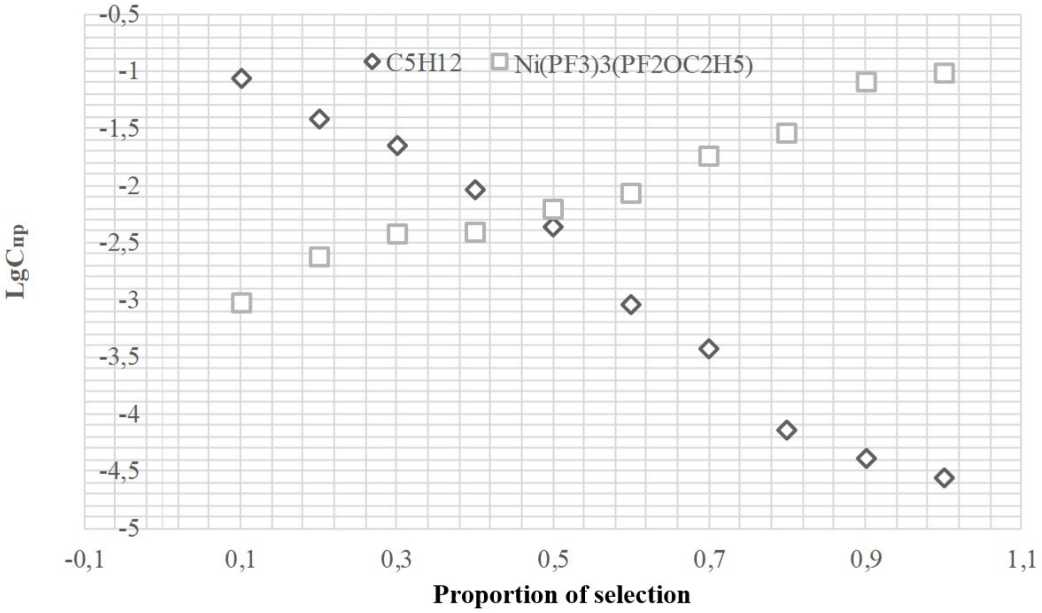

Fig. 2. Dependence of the logarithm of the impurity concentration on the fraction of the sampled substance for the $Ni(PF_3)_4$ - impurity system

Table 3. Results of non-volatile residue analysis

Element	C, atomic%	Element	C, atomic%
B	0.05	Cl	0.08
C	3.6	K	0.1
O	> 30	Ca	0.007
Na	0.05	Ti	0.01
Mg	0.0007	Mn	0.008
Al	0.02	Cr	0.08
Si	12	Fe	0.4
S	0.04	Co	0.0005
Cu	0.002	–	–

According to Table 3, the main chemical elements in the composition of the non-volatile residue are oxygen, silicon, and carbon. The presence of these chemical elements suggests SiO_2 as the main constituent compound of the residue sourced from the glass apparatus.

Conclusions and recommendations

We have determined liquid-vapour partition coefficients for impurities using the Rayleigh distillation method PF_3, n-C_5H_{12}, CH_2Cl_2, i-C_5H_{12}, 3-ethylhexane, 3-methylhexane, $Ni(PF_3)_3(PF_2OC_2H_5)$, n-C_7H_{16}, 2,2-dimethylhexane. Using the distillation method, we obtained a sample of high-purity $Ni(PF_3)_4$ with the content of molecular impurities of phosphorus fluoride, dichloromethane, alkanes, $Ni(PF_3)_3(PF_2OC_2H_5)$ at the level of $n\cdot10^{-3} – n\cdot10^{-5}$ mol% and impurities of chemical elements at the level of $n\cdot10^{1} – n\cdot10^{-5}$ ppmw.

References

1. **Makhatadze G.V., Schiller M., Bizzarro M.** High precision nickel isotope measurements of early Solar System materials and the origin of nucleosynthetic disk variability. *Geochim. Cosmochim. Acta*, 2023, 343, 17-32. DOI: 10.1016/j.gca.2022.12.020.
2. **Baranov V.Yu.** Isotopes: properties, production, application. M.: FIZMATLIT. 2005, 600 p. (In Russian).
3. **Klein C.B., Costa M.** Handbook on the Toxicology of Metals (Fifth Edition). *Volume II: Specific Metals*, 2022, 615–637.
4. **Khorasanov G.L., Ivanov A.P., Blokhin A.I., Demin N.A.** High- nickel steels depleted with nickel-58 isotope for fast reactor fuel element cladding. *Vopr. atom. nauki i tekhniki. Seriya: Materialovedenie i novye materialy [Issues of Atomic Science and Technology. Series: Material Science and New Materials]*, 2006, 2(**67**), 229-232 (in Russian).
5. **Uhm Y.R., Choi B.G., Kim J.B., Jeong D.H., Son K.J.** Study of a betavoltaic battery using electroplated nickel-63 on nickel foil as a power source. *Nucl. Eng. Technol.*, 2016, 48(**3**), 773-777. DOI: 10.1016/j.net.2016.01.010.
6. **Kharitonov I.D., Mazgunova V.A., Babain V.A., Kostylev A.I., Merkushkin A.O., Shemukhin A.A., Balakshin Y.V., Kozhemyako A.V., Kalmykov S.N., Magomedbekov E.P.** CVD-technology of production of Ni-based atomic sources. *Radiokhimiya [Radiochemistry]*, 2018, 60(**2**), 143-147 **(in Russian).**
7. **Baldokhin Y.V., Perfiliev Y.D., Kulikov L.A., Burnazyan M.A.** Oxidation of iron with different isotope content. *Vestnik Moskovskogo universiteta. Ser. 2. Khimiya [Bulletin of Moscow University. Ser. 2. Chemistry]*, 2015, 56(**2**), 91-97 (in Russian).
8. **Asadulin R.S., Galkin D.E., Maslov A.E., Palienko A.A., Sovach V.P., Tukhvatullin V.K., Ushakov A.A.** Patent RU No. 2748573 C1, 2021.
9. **Orlov, A.A.; Ushakov, A.A.; Sovach, V.P.** Separation of nickel isotopes in the process of filling a cascade of gas centrifuges with different number of stages. *TOKhT*, 2019, 53(**2**), 146-151. DOI: 10.1134/S0040357119020131 (in Russian).
10. **Merkulov I.A., Tikhomirov D.V., Obedin A.A., Zhabin A.Y., Paretskova S.A., Tomarev A.N., Kudrina Yu.V., Grigorieva V.A.** Patent RU No. 2650955 C1, 2018**.**
11. **Sozin, A.Yu., Chernova, O.Yu., Sorochkina, T.G., Troshin, O.Yu., Bulanov, A.D.** Identification of impurities in tetrakis(trifluorophosphine) nickel using chromatography-mass spectrometry. *AiK*, 2018, 22(**3**), 253-258. DOI: 10.15826/analitika.2018.22.3.010 (in Russian).
12. **Alekseev A.V., Yakimovich P.V., Kvachenok I.K.** Determination of impurities in nickel by ICP-MS. *Trudy VIAM [Proceedings of VIAM]*, 2020, 2(**86**), 101-108. DOI: 10.18577/2307-6046-2020-0-2-101-108. Available at: https://elibrary.ru/item.asp?id=42392009 (accessed 29.01.2025) (in Russian).
13. **Toporov Y.G., Tarasov V.A., Romanov E.G., Kazakov L.L., Andreev O.I., Andreychuk N.N., Kornilov A.S., Rotmanov K.V.** Obtaining of nickel-63 for current sources**.** *Sbornik trudov AO GNTs NIIAR*, 2018, 2, 34-40 (in Russian).

14. **Prusakov V.N., Petrov Y.V., Simonov N.F., Khrustalev B.V.** Patent SU 1061391, 1987.
15. **Otopkova P.A., Potapov A.M., Suchkov A.I., Bulanov A.D., Lashkov A.Yu.** Application of internal standard in isotopic analysis of highly enriched silicon-28 by high-resolution inductively coupled plasma mass spectrometry. *AiK*, 2021, 25(**2**), 98-109. DOI: 10.15826/analitika.2021.25.2.009 (in Russian).
16. **Troshin O.Yu., Bulanov A.D., Chernova O.Yu.** Liquid–Vapor Equilibria in the $SiCl_4$–A (A = $SiCl_4$–nFn (n = 1–4) Impurity) Systems. *Inorg. Mater*., 2018, 54, 840-843. DOI: 10.1134/S0020168518080162.
17. **Devyatykh G.G., Yelliev Yu.E.** Deep purification of substances. Textbook for universities. Moscow: ‘Higher School’. 1974, 160 p. (In Russian).
18. **Kovalev I.D., Potapov A.M., Bulanov A.D.** Measurement of isotopic composition of isotope-enriched silicon and its volatile compounds by laser mass spectrometry. *Mass-spektrometriya [Mass Spectrometry]*, 2004, 1(**1**), 37-44 (in Russian).

Received 19.12.2024
Approved after reviewing 27.01.2025
Accepted 05.02.2025