

## Decomposition of organic impurities in sodium iodide

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The decomposition process of organic impurities present in the initial sodium iodide raw material has been studied using mass spectrometry. The decomposition has been found to result in formation of CO, CO<sub>2</sub>, and various hydrocarbons. The decomposition of organic impurities is accompanied also by release of water that may be due both to direct decomposition of organic compounds and to oxidation thereof with oxygen present in the gas medium. Realization of the organic impurity oxidation at 400 to 450°C provides the complete removal thereof from sodium iodide.

Масс-спектрометрическим методом изучен процесс разложения органических примесей, присутствующих в исходном сырье йодида натрия. Установлено, что в результате их термического разложения образуется CO, CO<sub>2</sub>, углерод и углеводороды различного состава C<sub>n</sub>H<sub>m</sub>. Процесс разложения органических примесей сопровождается также выделением молекул воды, образование которых может быть связано как непосредственно с их разложением, так и их окислением в газовой среде кислородом. Проведение окисления органических примесей в диапазоне температур 400–450°C позволяет полностью удалить их из йодида натрия.

Activated alkali halide NaI(Tl), CsI(Tl), CsI(Na) scintillators and non-activated CsI crystals are used most widely to detect ionizing radiation. These crystals are grown by Kyropoulos and Stockbarger-Bridgeman methods [1]. At present, the large high-quality crystals (up to 500 kg mass) are obtainable with reproducible scintillation and optical parameters. The scintillation parameters of these crystals depend to a considerable extent on the impurity level (in particular, on that of oxygen-containing ones, such as carbonates, oxides, hydroxides, sulphates, silicates, phosphates, and iodates). The presence of oxygen-containing impurities in sodium and cesium iodide crystals among causes of the crystal trans-

parency deterioration, due both to the increased light absorption and scattering on impurity inclusions [2]. In the first case, the deterioration of the scintillation parameters is caused by reduced efficiency of energy transfer from the lattice to active luminescence centers and thus by reduced luminescence yield while in the second case, by light losses in the scintillator itself in the course of light transfer to photoreceiver [3–6]. The reduction of the hydroxides, oxides, iodates, and carbonates concentration in NaI(Tl) crystals provides the scintillation output enhanced by two and more times and resolution improved by 5–6 % [2, 3].

The impurity level in the crystals is defined by two factors, namely, by the raw

material quality and physicochemical conditions of crystal growth. The main fraction of impurities is present initially in the feedstock. Their content is regulated by standards and is defined by characteristics of the initial salt synthesis and purification processes. The reduction of the oxygen-containing impurity content in the alkali halide feedstock is an actual problem that is most critical in the production of initial sodium iodide salt. Due to specificity of industrial synthesis of sodium iodide, up to  $5 \cdot 10^{-3}$  mass % of organic impurities (in terms of carbon) and up to 1 mass. % of water as  $\text{NaI} \cdot 2\text{H}_2\text{O}$  crystalhydrate are present in the salt (according to analysis results). To provide the good crystals, it is necessary to purify the salt from organic compounds and water. Now, the salt is de-watered by heating in vacuum under continuous pumping-off, while the organic compounds are pyrolyzed at  $530\text{--}560^\circ\text{C}$  with formation of carbon followed by burning-out of the latter at the same temperatures using oxygen as dried air.

Another source of sodium iodide pollution with oxygen-containing impurities is air. In contact with air in usual climatic conditions, sodium iodide easily adsorbs water forming  $\text{NaI} \cdot 2\text{H}_2\text{O}$  crystalhydrate. Its dehydration at elevated temperatures is accompanied by hydrolysis of sodium iodide resulting in formation of oxygen-containing impurities. Besides, sodium iodide can interact at high temperatures with oxygen-containing components of air (oxygen and carbon dioxide), which also is accompanied by formation of oxygen-containing impurities [1]. The behavior of sodium iodide with respect to oxygen-containing components of air follows the one-component stability principle. That is, sodium iodide is active only with respect to pairs of impurities, and on the contrary, it is chemically stable against single components of air [7, 8]. However, it is very difficult to provide the required conditions of one-component system in the mass production. On the one hand, the salt contains water as crystalhydrate, so its heating is accompanied with the salt hydrolysis. Besides, the feedstock includes a phase containing hydroxyl groups, its decomposition under heating results in water release within two temperature ranges ( $180\text{--}280$  and  $280\text{--}400^\circ\text{C}$ ) [9, 10].

On the other hand, the raw salt always contains organic impurities. Their decomposition results in formation of carbon. The organic impurities are considered as hydro-

carbons of various compositions. The carbon obtained due to decomposition of organic compounds is burned out by oxygen of dry air at  $530\text{--}560^\circ\text{C}$  with  $\text{CO}_2$  formation. Thus, the system with oxygen-containing components is multi-component as a rule. The contact of sodium iodide with dry air at  $530\text{--}560^\circ\text{C}$  will be accompanied by the salt hydrolysis and accumulation of oxygen-containing impurities. As the decomposition of organic compounds proceeds at high temperatures, at which sodium iodide is hydrolyzed easily, and the composition of organic impurities may vary qualitatively and quantitatively, it is expedient to optimize the decomposition process of organic compounds and oxidation of carbon in sodium iodide. However, there are no literature data on decomposition process of organic impurities present in sodium iodide or other metal halides. The purpose of this work is to study the decomposition in vacuum of organic impurities in sodium iodide.

As the initial material, special purity sodium iodide produced by JE "Techniod", Saki (Ukraine). The initial samples of 100 to 150 g mass were poured into quartz ampoules, which were placed in a furnace with Nichrome heater. The ampoule with the sample was pumped out to the utmost pressure  $(3\text{--}5) \cdot 10^{-2}$  Torr by a roughing-down pump and then heated to  $600^\circ\text{C}$  at a rate of  $50$  to  $100^\circ\text{C}/\text{h}$ . Using a valve in the vacuum system, gas from vacuum system was sampled in the chamber of a mass spectrometer. During the sodium iodide heating, the gas atmosphere composition was recorded using an IPDO-2 partial pressure indicator of Omegatron type.

The gas medium being pumped out of sodium iodide samples consists of the following components:  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ . At heating, release of hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ) as well as compounds of organic nature with molecular mass 60, 76, 80, 98 (referred to below as high-molecular organic gases) and unidentified composition. The initial nitrogen content in gas mixture in all measurements makes 30 to 35 mass. %. During the pumping-out,  $\text{N}_2$  content decreases gradually. From dynamics of nitrogen partial pressure change during heating of  $\text{NaI}$ , it can be concluded that nitrogen does not interact with solid sodium iodide and is the residue of the air atmosphere which the ampoule was initially filled with.

The variation of partial pressures of the gas atmosphere components at sodium iodide heating is shown in Figs. 1 and 2. It

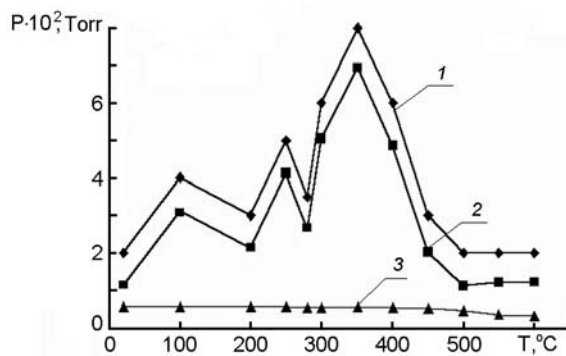


Fig. 1. Variations of the total (1) and partial pressure of water (2) and nitrogen (3) at heating of sodium iodide in vacuum.

follows from the data obtained that in the 70–130, 180–280, and 280–400°C ranges, water is released; in the 300–600°C range CO<sub>2</sub> and CO release is observed; in the 400–600°C range, hydrogen is released; in the 300–400°C range, the oxygen content is reduced; at heating above 200°C, the release of gaseous organic compounds is observed that becomes intensified considerably at heating above 300°C.

The release of water from the initial salt at heating in vacuum is related to presence of a phase containing hydroxyl groups in the initial samples [9]. The total pressure variation in the system practically is defined essentially entirely by water partial pressure (attaining 90–95 %), which concentration in the system prevails over other components. The release of gaseous organic compounds has a complex character. Fig. 3 illustrates the release process of organic compounds at heating of sodium iodide. It follows from these data that the heating of samples with organic impurities above 200°C in vacuum causes decomposition of organic impurities that is responsible for appearance of high-molecular gases in the gas phase. The content thereof increases continuously as the temperature is elevated and reaches a maximum at 500–600°C. Above 250°C, propane (C<sub>3</sub>H<sub>8</sub>) is revealed in the vacuum system are fixed. Above 350°C, the decomposition of organic impurities is accompanied by formation of methane (CH<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>). At 500–600°C, C<sub>2</sub>H<sub>2</sub> is formed. The content of light hydrocarbons increases at the temperature elevation.

It is possible to note, that CO and CO<sub>2</sub> are released in the same ranges as the gaseous organic compounds. Besides, the higher is the concentration of organic impurities in initial samples the larger CO<sub>2</sub> and CO amounts are. Basing on the above results,

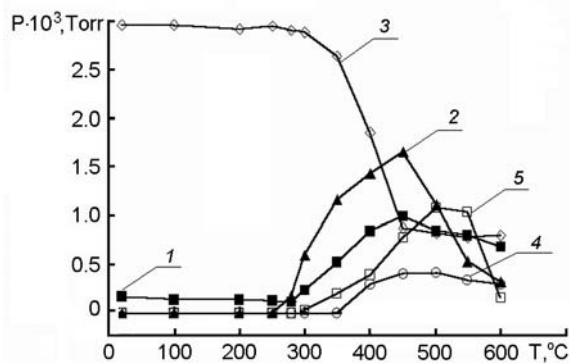


Fig. 2. Partial pressure variations of CO<sub>2</sub> (1), CO (2), O<sub>2</sub> (3), H<sub>2</sub> (4) and gaseous organic compounds (5) at thermal heating of sodium iodide in vacuum.

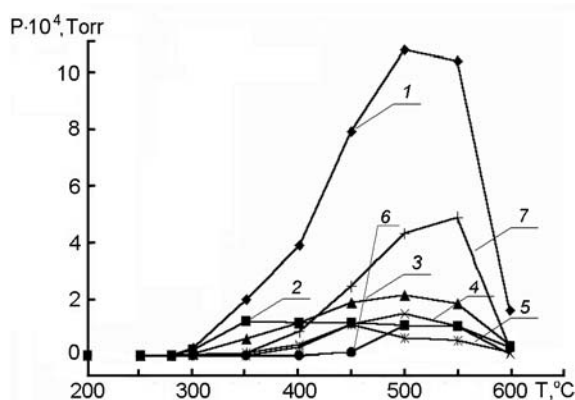
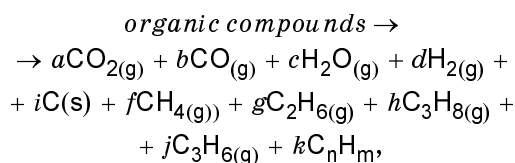


Fig. 3. Partial pressure variations of gaseous organic compounds being released at heating of sodium iodide in vacuum: total organic gases (1); high-molecular organic compounds (2); C<sub>3</sub>H<sub>8</sub> (3); C<sub>3</sub>H<sub>6</sub> (4); C<sub>2</sub>H<sub>6</sub> (5); C<sub>2</sub>H<sub>2</sub> (6); CH<sub>4</sub> (7).

the decomposition of organic impurities at heating in vacuum can be presented as follows:



where  $a, b, c, d, i, f, g, h, j, k$  are stoichiometric coefficients.

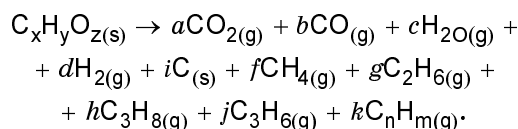
Since oxygen (5–6 mass %) is present in the system and its concentration decreases at heating of the salt, the release of carbon monoxide and dioxide may result from oxidation of organic impurities with oxygen. Knowing the composition of gas mixture, it is possible to calculate the mass of gas being pumped out per unit time:

$$P_i = 1.333P_{all}\omega_iV/RT,$$

where  $P_{all}$  is the total pressure in the system (Torr);  $\omega_i$ , the gas content in the mixture (per cent);  $V$ , the vacuum system volume ( $m^3$ );  $T$ ; temperature (K);  $R$ , the Boltzmann constant. The calculated contents of  $O_2$ ,  $CO_2$ ,  $CO$ ,  $H_2O$ ,  $H_2$  in the pumped stream are given in the Table. From the masses of pumped gases in the stream, it is possible to calculate amount of oxygen required to form  $CO_2$  and  $CO$  and to oxidize hydrogen, and to compare it to the observed variation of oxygen amount in the mixture. As the temperature varies within the 300–400°C range, the averaged changes of the  $CO_2$ ,  $CO$ ,  $H_2$  content in the stream (as determined by mass spectrometry) amount  $3 \cdot 10^{-6}$ ,  $3 \cdot 10^{-6}$ , and  $3 \cdot 10^{-7}$  g, respectively. Thus, about  $5.8 \cdot 10^{-6}$  g of oxygen is required for formation of  $CO_2$ ,  $CO$  and oxidation of hydrogen. The real change of the oxygen content in the stream makes about  $2 \cdot 10^{-6}$  g, thus, almost 3 times less than the required one. Besides, it is necessary to take into account that the carbon monoxide and dioxide are released also at 400–600°C, when no change of the oxygen content in the system is observed.

On the other hand, the oxygen may be supplied by sodium iodate present in the initial salt (up to  $10^{-3}$  mass % as determined by quantitative analysis), which is decomposed under heating with oxygen release into gas phase. The latter reacts with organic impurities forming carbon oxides and water. However, the decomposition of iodate can proceed at temperatures exceeding 450°C, while the  $CO_2$  and  $CO$  release is observed at lower temperatures. Thus, the  $CO_2$  and  $CO$  release is not related to the

oxidation of organic compounds with air oxygen (at least, if this process takes place, its part in formation of those components in the 200–400°C temperature range does not exceed 30 % and at higher temperatures it can be neglected at all). The formation of  $CO_2$  and  $CO$  is associated with decomposition of organic impurities. This statement is evidenced by the fact that decreasing of partial pressure of oxygen in the system occurs as a rule when the hydrogen release starts. At decomposition of organic compounds above 400°C without pumping-out, no oxygen was revealed in the gas medium and an intense hydrogen release started. It is possible that all oxygen is spent to oxidize hydrogen, and the excess hydrogen is recorded by the mass spectrometer. The change of water content in the pumped-out gas stream due to water formed by hydrogen oxidation with oxygen is less than 0,1 mass % of the total water amount in the gas mixture. As the decomposition of organic impurities is accompanied by  $CO_2$  and  $CO$  release, those must contain oxygen along with carbon and hydrogen, and the decomposition reaction must run like the equation

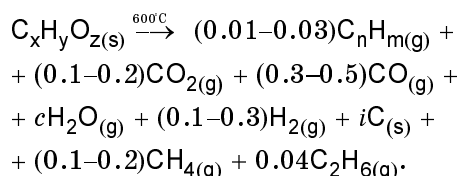
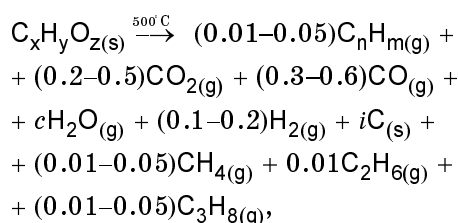
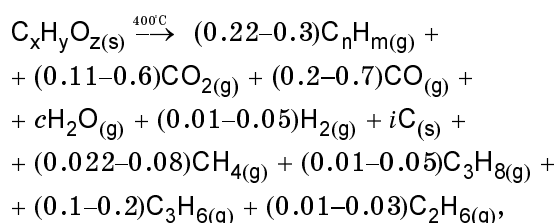
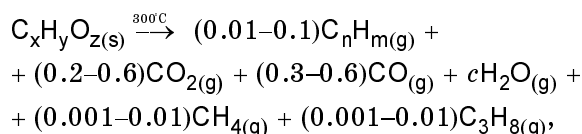
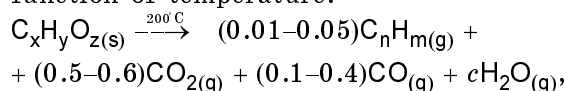


It is possible that the organic compounds have more complex composition and contain other elements such as nitrogen, phosphorus, sulfur, etc. These elements could be revealed in the released high-molecular gases (with molecular masses exceeding 60). However, their part will be several times lower as compared to the released oxygen-containing compounds, and thus, the influence of oxygen-containing gases  $CO_2$ ,  $CO$

Table. Calculated amounts (g) of  $O_2$ ,  $CO_2$ ,  $CO$ ,  $H_2O$ ,  $H_2$  in the gas stream pumped-out at heating of sodium iodide

$T, ^\circ C$	Mass of pumped gas in the stream, g				
	$CO_2$	$CO$	$O_2$	$H_2O$	$H_2$
20	$(2-4) \cdot 10^{-6}$	$(2-3) \cdot 10^{-6}$	$(1-1.2) \cdot 10^{-5}$	$(2-4) \cdot 10^{-5}$	$(2-4) \cdot 10^{-7}$
200	$(2-3) \cdot 10^{-6}$	$(1-3) \cdot 10^{-6}$	$(5-6) \cdot 10^{-6}$	$(3-4) \cdot 10^{-5}$	$(6-8) \cdot 10^{-8}$
300	$(3-6) \cdot 10^{-6}$	$(3-6) \cdot 10^{-6}$	$(2-4) \cdot 10^{-6}$	$(1-3) \cdot 10^{-4}$	$(4-5) \cdot 10^{-8}$
400	$(6-8) \cdot 10^{-6}$	$(7-10) \cdot 10^{-6}$	$(1-3) \cdot 10^{-6}$	$(1-20) \cdot 10^{-4}$	$(3-5) \cdot 10^{-7}$
500	$(6-8) \cdot 10^{-6}$	$(8-10) \cdot 10^{-6}$	$(1-2) \cdot 10^{-6}$	$(5-7) \cdot 10^{-5}$	$(2-4) \cdot 10^{-7}$
600	$(5-8) \cdot 10^{-6}$	$(5-7) \cdot 10^{-6}$	$(1-2) \cdot 10^{-6}$	$(5-7) \cdot 10^{-5}$	$(2-4) \cdot 10^{-7}$

and H<sub>2</sub>O will prevail. As the temperature elevates, the decomposition of organic compounds proceeds with formation of lighter gases. The calculation of amounts of released organic gases has allowed us (without taking into account the carbon forming in the solid phase and possible formation of water at decomposition of organic impurities) to estimate the molar content of components in the mixture formed due to decomposition of organic compounds as a function of temperature:



It is to note that the composition of the pumped-out gas depends not only on the content of organic impurities in the raw salt but also on the vacuum at which the decomposition is realized. As the pressure in the vacuum system increases, the concentrations of high-molecular organic compounds are increased at temperatures up to 400–500°C, while at higher temperatures, the part of pyrolysis with carbon formation rises. At 200, 250, 300, 350, 400, 450, 500, 550°C, experiments have been done on the burning-out of organic impurities with dry air oxygen. After holding at one of the specified temperatures in dry atmosphere

for 15–20 min, the salt in the ampoule was pumped up to the utmost vacuum, the gas stream composition was recorded, and then the temperature was raised up to 550–570°C under checking the pumped gas by mass spectrometer. As follows from the results obtained, the oxidation of organic impurities in the 200–350°C range is low-efficient. After oxidizing at 350–400°C, a small amount of organic gases (less than 0.05 %) is observed in the gas mixture. The oxidation in the 400–450°C temperature range provides a complete removal of organic components from the initial salt. The concentration of organic impurities in sodium iodide after oxidation makes less than 10<sup>-3</sup> mass % (as carbon), thus providing the crystals without carbon inclusions.

Basing on the experimental results, the following conclusions can be drawn. The organic impurities in the initial sodium iodide contain oxygen besides of carbon and hydrogen, the composition thereof can be expressed by a conditional formula C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>. The decomposition of organic compounds proceeds according to a complex reaction scheme that depends on composition of organic compounds and the decomposition conditions. As a result of the decomposition, formed are carbon, hydrocarbons of various compositions C<sub>n</sub>H<sub>m</sub>, CO and CO<sub>2</sub>. The decomposition of organic impurities is accompanied by water release. It may be formed directly due to decomposition of organic compounds as well as due to the oxidation thereof with oxygen present in system. The organic impurities can be completely removed from sodium iodide intended for single crystal growing by oxidizing those at 400–500°C. When treating the initial sodium iodide, it is necessary to take into account the salt interaction with oxygen-containing impurities, since it is impossible to realize an one-component system. The gas atmosphere contains residual amounts of carbon dioxide, oxygen and water. The water and carbon dioxide may stimulate the sodium iodide decomposition.

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## **Розклад органічних примесей, що містяться у йодиді натрію**

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Методом мас-спектрометрії проведено дослідження процесу розкладу органічних примесей, що містяться у йодиді натрію. Встановлено, що в результаті їхнього термічного розкладу формуються CO, CO<sub>2</sub>, вуглець та вуглеводневі речовини різного складу C<sub>n</sub>H<sub>m</sub>. Процес розкладу органічних примесей супроводжується також виділенням молекул води, утворення яких може бути пов'язано як з їх безпосереднім розкладом, так і з окислюванням присутнім у газовому середовищі киснем. Проведення окислення органічних сполук у температурному діапазоні 400–450°C дозволяє повністю вилучити їх з йодиду натрію.