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Purification of Iodine by Crystallisation from a Hydrogen Polyiodide Solution and Check of its Contamination Level

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Substantial quantities of iodine may conveniently be purified by saturating a 10 M hydrogen iodide solution with iodine, and precipitating it in microcrystalline form by dilution with water. The non-hygroscopic iodine crystals are filtered, washed and dried at room temperature.

The trace impurity and water contents may reliably be determined by potentiometric, mass spectrometric, radiometric and IR spectrometric methods developed for this purpose. The total amount of foreign substances has always been found to be less than 0.01 %. Alkaline iodine stock solutions may be preserved and sampled without losses for one year or longer.

The several iodine batches prepared are intended to be employed in quantitative analysis and to study the solution chemistry of iodine.

Iodine is known to be an exceptionally rapid oxidizing agent, a fact that results in the introduction of impurities, unless precautions are taken to avoid every contact with reducing substances throughout its preparation and handling.

Classical purification methods involve, for instance, distillation with water vapour and repeated sublimations in a nitrogen stream. In these operations stopcock grease, dust, mineral oil or mercury and other detrimental substances are unavoidable; moreover purification of large amounts of iodine requires some effort. Hence a simpler method of purification was sought for.

For this purpose one may utilize the fact that iodine is highly soluble in concentrated alkali or hydrogen iodide solutions where it forms multiple charged polynuclear ions. When such a solution is diluted with water, iodine crystals precipitate, while the main impurities are unaffected and remain dissolved.

Hydrogen iodide offers, from the preparative point of view, the important advantage that it dissolves more iodine than an equimolar potassium iodide solution, because the H^+ ion is a much less efficient salting out agent than the big alkali cation. To estimate the efficiency of this approach a series of trace analytical methods were developed. The problems arising when iodine solutions have to be prepared, preserved and sampled without losses are also treated in some detail in the present article.

Iodine purification by precipitation upon dilution is a method which was discovered more than a hundred years ago (1865) by Jean Servais Stas[1–3] (*cf.* also Gmelin[4]) who refined it so far that he was able to obtain a fairly correct value for the atomic weight of iodine (126.80). However, Stas employed potassium iodide solutions as solvent, and subjected the precipitated iodine to sublimation, which was believed to result in an improved purification. The present investigation is based on Stas' pioneering research, and the proposed procedure represents an improved version of his method.

METHOD

The present approach is based on the rapid establishment of equilibria of the general type

$$p\,I_2(s)+q\,I^- \rightleftharpoons I_{2p+q}^{q-} \qquad (1)$$

where p and q represent integers greater than unity. According to our preliminary solubility data the predominating iodine bearing species,

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besides I_3^-, is a triply charged anion which may have the composition I_{17}^{3-} at low [3 M Na^+ (ClO_4^- + I^-)], and I_{12}^{3-} at high [10 m Na^+ (ClO_4^- + I^-)] ionic strengths. It is clear from eqn. (1) that the quotient $[I_{2p+q}^{q-}]/[I^-]$ (=the dilution condition) will be constant only if $q=1$. The concentration of polyiodide ions must decrease with $[I^-]^q$ (=the equilibrium condition). Thus iodine crystals will be precipitated when a saturated hydrogen iodide solution is diluted with water ($q=3$). Fortunately the most likely contaminants, chloride and bromide, appear to form only single charged polyhalogenide ions ($q=1$), and they remain in solution.

Before entering the description of the purification procedure in detail, it appears appropriate to summarize the *principles* guiding our choice of experimental conditions.

(a) Only gases and liquids purifiable by distillation are used: hydrogen iodide and water. In the final stage of the preparation oxygen is employed to remove the last traces of HI adhering to the iodine, thereby more iodine is formed.

$$O_2+4H^++4I^-\rightarrow 2H_2O+2I_2 \qquad (2)$$

(b) All steps of the purification are carried out at room temperature. It is therefore easy to protect the iodine solution and the crystals from the laboratory atmosphere with carbon dioxide. This gas is required to prevent decomposition to iodate and iodide.

(c) The degree of supersaturation, when precipitating, is kept at a minimum by vigorous stirring and dropwise addition of water. This was done in order to suppress the amount of mother liquor occluded.

(d) The materials come into contact only with glass and platinum. The solubility of pyrex glass in our acidic solutions must be very low. The crystals are transferred with a platinum spoon.

(e) Several *model experiments* were made with the most likely impurities. In order to check the degree of purification the radioactive tracers $^{36}Cl^-$ and $^{14}CN^-$ were added. (No suitable Br^- isotope is available). These experiments have shown that by a single precipitation 99.8 % of the chloride ions and 98 % of the cyanide ions are removed. It should be recalled that ICI, IBr and ICN cannot be eliminated with sublimation.

(f) Finally it should be pointed out that the iodine in the filtrate may easily be recovered by using, for instance, hydrogen peroxide, oxygen or ozone[5] as oxidizing agent. The advantage of using these oxidants is that no foreign substances are introduced.

PROCEDURE

Purification of 1 kg of iodine with a yield of 60 %.

General. One kg of iodine (8 mol) and 190 ml (373 g) 10 M (fuming) hydrogen iodide solution are mixed in a beaker covered with a watch glass. The dissolution is endothermic, and the beaker should therefore be warmed on a water bath to keep the solution temperature at about 25 °C in order to maintain a high solubility of iodine.

The vapour pressure of hydrogen iodide is considerable at 25 °C and elevated temperatures should be avoided in order to reduce losses. This and the following manipulations should therefore be carried out in a well ventilated hood.

Next, the resulting dense solution, with a metallic lustre, is filtered through a sintered glass filter to remove the floating insoluble material that is usually present in commercial products and any iodine crystals that may remain undissolved.

The precipitation of iodine is carried out in a tall beaker (5 or 10 l). Water is added dropwise from a burette, while the suspension is agitated vigorously. When the starting volume has been increased ten times the additon of water may be stopped. Further dilution brings about only a negligible increase in yield.

The small iodine crystals were gathered in a specially constructed filter funnel illustrated in Fig. 1. With this funnel we could easily wash and dry the iodine crystals in a protective atmosphere of carbon dioxide.

The washing procedure was first monitored by control of the pH of the filtrate, then by estimating the $[I^-]$. When the pH had increased to about 4, the washing continued until addition of Ag^+ to the filtrate yielded a colloidal suspension of AgI(*s*) equal in scattering power to that of an acid saturated iodine solution to which silver ions had been added.

The crystals were finally dried in a desiccator provided with extruded molecular sieves, (the moist crystals contained about 2 weight % water).

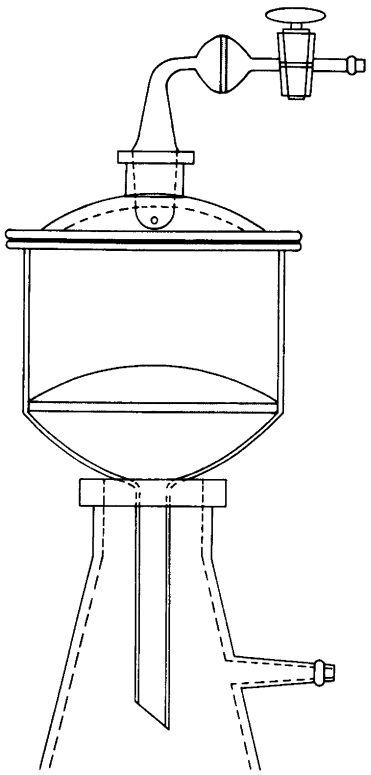

Fig. 1. The edge of a commercial glass filter funnel is bent to a rim, and ground flat to fit the cover of a desiccator. The funnel is used for washing the iodine crystals. The washings are removed by applying a slight underpressure in the filtering flask. CO_2-gas, free from dust, replaces the withdrawn water.

The desiccator was exhausted, and the iodine was left to dry for a few days. It was then filled with oxygen to remove the last traces of HI. Violet iodine vapours became visible at once due to the reaction (2). A new portion of molecular sieves was then introduced to absorb the water formed.

After this step the iodine is ready for use. The yield was generally about 600 g of dry material.

The washings, containing H^+, I^- and I_3^-, were collected for recovery of iodine by oxidation with hydrogen peroxide.

Comments. It would have been preferable to remove the excess water from the crystals by centrifugation. However, the iodine crystals are so soft that they agglomerate. The resulting mass is difficult to remove and, by grinding, new impurities are easily introduced.

We have been using starting materials of *pro analysi* quality. However this procedure has proved to be so efficient that less expensive qualities would have served equally well. As the iodine in the filtrate and the washings are easily recovered, our procedure may be regarded as a fast, convenient and cheap method of purifying iodine.

PREPARATION OF STABLE IODINE STOCK SOLUTIONS

Iodine has a high vapour pressure at room temperature. Hence, some precautions have to be made when the samples are weighed.

This problem has been encountered by several generations of analysts and many proposals have been made to solve it. These are critically surveyed by Kolthoff and Belcher.[6] The problem was recently reconsidered by Bower[7] who suggested the use of a special apparatus. The most common approach is to dissolve iodine in a potassium iodide solution.[6,8,9] This method could not be employed in our case as the iodine stock solutions were used in both oxidation and reduction experiments. We propose a simple approach – dissolution of iodine in alkali and weighing of this solution.

Iodine dissolves readily in a small excess of sodium hydroxide and the disproportionation

$$3\,I_2 + 6\,OH^- \rightarrow IO_3^- + 5\,I^- + 3\,H_2O \qquad (3)$$

is completed within a few hours as can be seen by the discoloration of the solution. Since this reaction is perfectly reversible, we used throughout this project alkaline iodine stocks.

The only disadvantage of the proposed method arises from the need of reacidification to recover I_2. When iodine participates in a classical iodometric reaction, a final readjustment of the pH may also be required to avoid the oxygen error.

Our stock solutions have in each case been found to maintain their iodine content for periods as long as one year, even though samples often were withdrawn.

We have also tried several organic solvents such as carbon tetrachloride, benzene, ethylene glycole and silicone oil to prepare stable iodine solutions. However, all of them were found to contain substantial amounts of redox impurities and had therefore to be discarded.

A convenient method was developed to determine traces of *redox impurities* in alkali hydroxide preparations. The sample was added to an HBr solution with a small but known excess of Br_3^-. The change in Br_3^--excess was determined and taken to equal the amount of redox impurities. The analyses were carried out as described in a following publication[10] dealing with the coulometric oxidation of iodine.

In a typical case the sodium hydroxide originating from the Merck Co ("Suprapur") contained 15 μeq oxidizing impurities per mole. Our own preparations (from sodium) of about the same quality were also tested.

The weighing procedure. The iodine stocks were prepared by determining the weight increase upon introducing as quickly as possible (*e.g.*) 50 milliequivalents (6.35 g) of I_2 into a pyrex flask containing (*e.g.*) 200 ml CO_2- and O_2-free 0.28 M NaOH-solution (about 10 % excess of OH^-). The flask contained a teflon covered magnetic bar and had an ungreased glass stopper. This was replaced with another slightly greased stopper after all the iodine had left the surface. The whole dissolution procedure took about one hour. The complete disproportionation required a few additional hours.

This procedure involves the weighing of objects of several hundreds of grams with a precision of about 0.1 mg. Hence a high quality balance is required, and attention must be paid to ensure that the vessel attains equilibrium with the moisture of the air in the balance room. A thermostated balance room is therefore necessary.

In each case the proper correction for the buoyancy of air was applied.

It should be added that the stopcocks of the weighing burettes used for sampling must fit precisely. Otherwise the slight underpressure which develops by carbon dioxide absorption from the air left in the burette, causes a drift of about 0.05 mg/min because of intrusion of external air.

DETERMINATION OF FOREIGN SUBSTANCES AND IMPURITIES IN THE IODINE PREPARATIONS

General. The several iodine batches prepared are intended for use as standards in quantitative analysis and in redox equilibrium measurements.

To test whether they are suitable for these purposes, we have developed a method to determine trace amounts of hydrogen iodide in the iodine phase. Water was analysed with the IR spectroscopic method developed by Farrow and Hill.[11] A precision of a few parts per 10^5 iodine was obtained in these analyses. A further important task has been to look for *unsuspected* contaminants which might have been introduced in the course of the preparation, or co-precipitated with the iodine. As will be discussed in more detail below, the amount of non-volatile impurities was in each case found to be less than 4 parts per 10^5. One might therefore be inclined to think that the content of foreign non-volatile substances could be reduced by sublimation.

This is indeed a common purification approach. Effective sublimation will require an elevated temperature and a large volume of a streaming gas (or exhaustion). Thereby it is unavoidable to expose the iodine to *uncontrollable* volatile and other impurities.

It seems therefore preferable to analyse iodine for foreign substances and to apply the relevant correction when necessary. A similar approach has proved to be useful for other materials as well, *e.g.* NaI, Fe_2O_3 and sulfur.

The sublimation residue. This test was primarily made to find the amount of dust originating from the incompletely filtered gases and from the air, when the iodine was handled.

Samples of five or ten grams of iodine were weighed into boats made of fused silica. These were then placed in a quartz combustion tube. A narrow zone was heated externally to about 100 °C while a slow stream of purified and filtered nitrogen passed through. A blank experiment was made simultaneously. In the majority of cases a *weight decrease* varying between 0.01 to 0.29 mg was found. The weight of the empty boat (the blank) decreased by 0.05 to 0.34 mg.

To get an estimate of the upper limit for the non-volatile substances, we may consider the experiment with a sample of 5.11 g iodine. A weight increase of 0.14 mg was observed, while the empty boat lost 0.05 mg. Hence we can set the maximum residue to 0.19 mg. The non-volatile residue is thus certainly less than 4 parts per 10^5.

In order to improve the precision of this test, a material with better weight stability than quartz is needed. The commercial quartz boats were found to lose a few parts per 10^6 of their mass in each heating period. This effect might be due to a changed amount of adsorbed gases in the pores.

The mass spectrographic study. A mass spectrograph of the type "Spark Source MS, AEI MS 702" was employed to detect traces of compounds with a mass number exceeding 14. The iodine samples were ground together with graphite in an agate mortar, and small electrodes were made from the mixture.

Only three foreign elements could be discovered: Si, Na and S. An attempt was made to estimate their concentration level, and we obtained the following estimates: (mol ratio $\times 10^4$):

Si=5, Na=0.15, S=0.1.

A considerable part of the iodine sample evaporated between the sweeps, so these figures may be regarded as semiquantitative only. No traces of Cl, Br, Al or Fe were found. We would like to point out that a part of the observed intensity (maybe even the whole) for Si and S might be due to the presence of N_2^+, and O_2^+ in the spectrometer. The starting material (a commercial preparation of *pro analysi* quality) was analysed in the same way; and the following approximate results were obtained: (mol ratio$\times 10^4$):

Si=10, Na=2.5, S=1, Al=5, Fe=0.2.

Thus a considerable purification from all elements except silicon could be achieved in a single precipitation step.

However, we doubt the results for this element because these amounts of silicon dioxide should easily be detected in the evaporation experiments. Perhaps some contamination with SiO_2 occurred when the iodine sample was pulverized in the agate mortar. Alternatively its intensity is overestimated. Wartenberg [12] (*cf.* also [13]) studied this question systematically and found that abrasion from an agate mortar may contaminate the product considerably.

The hydrogen iodide content. Because of our method of preparation it was necessary to determine the amount of occluded hydrogen iodide in the washed, oxidized and dried product.

This was done by measuring the increase of hydrogen ion concentration when the iodine sample was introduced into a (2 M NaCl+1 M NaI) solution containing a small, but exactly known, proton excess.

The sodium iodide was added to dissolve the large amount of iodine (several grams) needed to get a high sensitivity. With the method described one may conveniently determine 0.5 μmol of HI which corresponds to a hydrogen iodide mol fraction of less than 10^{-5}. The hydrogen ion concentration of the NaCl–NaI solution was first adjusted by coulometric reduction of water using a Wilhelm bridge as anode compartment.

About 0.5 mM iodine was added before the coulometric titration in order to remove the redox impurities present.

The hydrogen and triiodide ion concentration were determined after each step of electrolysis by measuring the emf of a glass electrode and a platinum redox electrode *versus* a common external reference electrode.

The emfs of these cells may under the present conditions (25 °C) be expressed by the simple equations:

$$E(\mathrm{GE}) = E_0(\mathrm{GE}) + 59.16 \log h \quad (4)$$

$$E(\mathrm{Pt}) = E_{01}(\mathrm{redox}) + 29.58 \log [I_3^-] - 88.74 \log [I^-] \quad (5)$$

$$\cong E_{02} + 29.58 \log [I_3^-] \quad (6)$$

Here the E_0:s are isothermal constants and h stands for $[H^+]$. As the electrolysis proceeded, the current yield for the reduction of hydrogen ion steadily decreased, while the yield for the triiodide reduction increased.

Beyond 1 mM hydrogen ion concentration no significant further alkalification could be achieved as shown by the constant E(GE) and the successively decreasing E(Pt) values. At this point (pH=3) the electrolysis was interrupted, and air was passed through the test solution. Due to the reaction

$$O_2 + 4H^+ + 6I^- \rightarrow 2\,H_2O + 2\,I_3^- \quad (7)$$

a slow alkalification occurred which was stopped when h had dropped to about 50 μM (pH 4.3). At a lower concentration reversible emf value cannot be obtained in these unbuffered solutions.

In order to calculate the change in hydrogen ion concentration after the additions of iodine E_0(GE) had to be evaluated. This constant was estimated in two ways:

(1) From the set of values of E(GE), E(Pt) and w (mol of electrons introduced at the cathode) a computer made an iteration calculation of the two E_0:s assuming that the *combined* current yield was 100 %.

(2) After the iodine additions a few milliliters of 100 mM HCl were introduced. The emf change of the glass electrode was used to calculate E_0(GE). The two values only differed by a few millivolts.

Approximately one gram portions of the iodine sample were added to the NaCl–NaI solution whose hydrogen ion concentration was about 50 μM. After each addition the emf values were measured. The E(Pt) data thus obtained were used for the control of the computer value of E_{02}.

Also in this case the agreement was good. In a typical experiment 6 g of iodine were found to contain 0.6 μmol of HI, corresponding to a hydrogen iodide mol fraction 1.3×10^{-5}.

This is an estimate only. We ascribed the total E(GE) change (3 mV) caused by the dissolution of iodine to a change in h. The medium is varied by the additions of iodine, and, as about 50 % of the I^- ions are transformed to I_3^-, the activity factor of the hydrogen ions is changed.

For our present purposes this estimate of the hydrogen iodide content was considered satisfactory, but it may be much improved if the medium effects are estimated with the help of model experiments.

Drying of iodine and determination of its final water content. Because iodine is extremely sensitive to redox impurities, we attempted to remove the last traces of water at room temperature instead of melting. The latter procedure would make it necessary to grind the material.

Incomplete removal of water can easily be corrected for.

A series of model experiments were carried out to find the most suitable drying agent. The drying procedure was monitored by using water containing ^3H.[14] Iodine and potassium iodide were dissolved in the smallest possible amount of water.

Iodine was precipitated, washed and dried. In the exploratory experiments the tritium content in the solution corresponded to about 20 MBq/l and in the main series about 600 MBq/l to increase the sensitivity. HI was replaced by KI because of the high vapour pressure of HI.

In each case three samples were prepared as identical as possible to keep the quenching effects (the counting efficiency) on the same level. A non-active iodine blank was used as the reference, the active iodine followed, and another sample with active iodine plus a standard addition of tritiated water was finally counted.

The β counting of the tritium decay was carried out by using a liquid scintillator (ACS) from The Radiochemical Centre, Amersham, GB. A scintillation spectrometer, Packard model 3375, was used for the measurements. This instrument is provided with a special measuring channel for ^3H.

The iodine samples were dissolved in a deoxygenated 0.5 M NaOH solution containing 0.15 M N_2H_4. This solution dissolves iodine rapidly and a colorless solution is formed. Three drying agents were tested: molecular sieves (10 A), sulfuric acid and phosphorus pentoxide. The last two were dispersed in a silica carrier as supplied by the Merck Company. Our results are summarised in Table 1.

Table 1.

Sample No.	Drying agent	Weight % water
1a	Molecular sieves	$0.07_9\pm0.03$
1b[a]	Molecular sieves	$0.08_4\pm0.01$
2a	Molecular sieves	0.073 ± 0.002
3a	Molecular sieves	0.062 ± 0.002
2b	Sulfuric acid	0.016 ± 0.001
3b	Sulfuric acid	0.016 ± 0.001
2c	Phosphorus pentoxide	0.013 ± 0.001
3c	Phosphorus pentoxide	0.037 ± 0.001

[a] Sample 1b was removed after two days from the desiccator and placed into a vessel provided with tritiated water. The analysis was carried out two days later. Sample 1a was analysed at the same time, it had by then been dried for 4 d. The insignificant difference between the two water contents indicates that the hygroscopicity of iodine lies below the detection limit of this method.

In the desiccator provided with P_2O_5 a brown gas with a strong smell had evolved. Iodine probably had reacted with the phosphorus (III) acid impurity usually present in commercial preparations (Ref. 13, p. 353). This drying agent cannot therefore be used.

Some change had also occurred in the desiccator with sulfuric acid. The surface of iodine had formed a compact mass that had to be pulverised with a glass rod. Also in this case we suspect some volatile impurity (*cf.* Ref. 13, p. 352).

However, no change could be detected in the iodine crystals dried over molecular sieves. Although this desiccant seems to react rather slowly, it should be preferred. The drying period must be prolonged and the drying agent preferably renewed after some days.

The procedure finally adopted consisted of drying iodine over molecular sieves that had been heated to 200 °C and allowed to cool under vacuum. The iodine samples were placed in the desiccator, this was exhausted, oxygen was added and finally exhausted a second time as described in the procedure part.

To determine the water content in non-active samples we used the method of Farrow and Hill.[11]

Iodine was dissolved in dried bromine. The IR absorption between 4000–3100 cm^{-1} was measured using Infrasil cells. The water peaks at 3549 and 3647 cm^{-1} were measured. A typical preparation contained 0.014 weight % water in good agreement with the model experiments.

The combined figures for the HI- content and the residual water content indicate that the occluded water contains some hydrogen iodide (approximately 0.7 M). From this we conclude that the iodate content must be negligible.

The efficiency of the purification method. The metal ion impurities were seen from the mass spectrometric study to be reduced considerably with our method. It was also of interest to find the efficiency for the *removal of the negative ion impurities.* Chloride and bromide are common impurities in the commercial hydrogen iodide and iodine preparations, CN^- may be formed when iodine comes into contact with organic substances.

Cl^- and CN^- were used as model ions. Hence, ^{36}Cl and ^{14}CN were used as tracers. Iodine was dissolved and precipitated using radioactive water. KI was employed instead of HI to avoid losses due to volatilization of HCl and HCN. However, the precipitated iodine was washed with non-active water. It was dried in the same manner as described above.

Several independent series of experiments gave the result that the mol fraction of chloride in the iodine phase is about 1000 times lower than in the starting solution, while the cyanide mol fraction is reduced by a factor of 50.

The uncertainty of these conclusions may be estimated by the fact that the total activity (from the iodine and the washings) was found to amount to 106 % of the initial amount of ^{36}Cl activity, and to 95 % of the initial amount of ^{14}CN. The total amounts of tracers used were 300 kBq ^{36}Cl and 150 kBq ^{14}CN. 99.9 % of the total amount of Cl was found in the washings and 98 % of the total CN. The amount of chloride ions in the HI and I_2 preparations were assumed to equal their maximum values according to the specification from the supplier.

Hence we may have little doubt that the decomposition of the multicharged polyiodide complexes by dilution represents a quite efficient way of purifying iodine.

CONCLUSIONS

A single step of slow precipitation from a saturated 10 M hydrogen iodide solution appears to furnish an iodine phase with a contamination level which lies below 0.01 %. A more precise specification is difficult at present because of the uncertainties of trace analytical methods.

Drying with molecular sieves brings the water content down to a few hundredths of a percent within a few days as shown by tritium tracers. The exact value of the water content of a particular iodine sample is easily measured with infrared spectroscopy to within a few parts per 10^5.

Hence this monoisotopic, non-hygroscopic element, which may easily be transformed to a higher or lower oxidation state, may be regarded as an especially valuable analytical standard substance.

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