REVIEWS

DRYING AND WEIGHING OF PRIMARY STANDARD
REAGENTS FOR TITRIMETRIC ANALYSIS

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The fundamentals and the present status of titrimetric analysis are briefly discussed. The drying conditions for primary standard reagents recommended previously and some recent works are reviewed. The most advisable conditions and procedures for handling are given.

1. Introduction

Titrimetric analysis is one of the most suitable methods for the determination of a constituent of more than several %. The method is rather rapid compared with gravimetry, and gives precise results. A precision of nearly 0.1 % (relative) is obtainable by the usual procedure, and sometimes 0.02 % (relative) is possible by using a weight buret. Therefore, the method is still very important as the 'reference method'¹⁾ in practical analytical laboratories.

The results of nearly all instrumental methods are obtained by comparison of a signal from a component to be determined in a sample with that from the same component in a reference material of similar composition. The ratio of the two signals measured is multiplied by a factor which is the content of the component in the reference material. Therefore, the accuracy of the instrumental method depends on the content of the reference material used. On the other hand, the precision of the results depends on that of the instruments used, which consists of the sum of the precisions of the devices such as the activator or conditioner of the component, signal transducer, electronic amplifier and its current measuring device. Thus, it is very difficult to decrease the total error to less than 1 %, and the precision of the results of the instrumental method cannot be better than that of titrimetric methods.

For the results of a titrimetric analysis, the fundamental datum is the purity of the primary standard reagent (PSR) used for the standardization of the standard solution. The purities of many PSRs are measured precisely and accurately by the governmental institutes in many countries: for example, the Industrial Inspection Institute of Japan (IIIJ), the National Bureau of Standards in the U.S.A. (NBS), etc., within the error of 0.01 %. However, the methods used in IIIJ are the high precision titrimetry with a weight buret²⁾, by which the purities of the PSRs are obtained by relative comparison with the purities of

basic reference materials kept in the IIIJ²⁾. In this case, the materials construct a group of prototypes of titrimetric analyses in Japan, and their purities are certified by the comparison with one another and also with other reference materials (RMs) such as Standard Reference Materials from NBS. However, such a comparison process does not give the results which are traceable directly to the system of the SI units, and therefore titrimetric methods cannot be a 'definitive method'¹⁾.

The present author has already discussed this problem in previous reviews³⁻⁵⁾. That is : When the purities of PSRs are determined by precise gravimetry or by a precise coulometric titration, the results of titrimetric analyses become traceable to the system of the SI units, and the use of the latter method corresponds to acceptance of the Faraday constant as the international standard for titrimetric analysis. The acceptance was already recommended by Tutunzic⁶⁾ and more recently by IUPAC⁷⁾ as an international standard for 'analytical chemistry', and the opinion of the present author which supports the use of the constant as an international standard for 'titrimetric analyses' has been shown in the reviews in detail³⁻⁵⁾. Therefore, this problem is not discussed here further.

The other problem of the purities of PSRs is the disturbances by contaminants in atmosphere. All materials exposed to the atmosphere are always contaminated by moisture and other contaminants, and their purities decrease. The species and the amounts of such contaminants differ with laboratories and perhaps with weighing of the materials. Therefore, we have to make this error smaller than the weighing error of the balance used. For example, if one gram of PSR is weighed out with an error of 0.1 mg, the contaminants should be less than 0.01 %, which is a very difficult level to attain. This problem is not so serious on the purity measurements worked in IIIJ, because the purity of PSR is measured by the relative comparison with the purity of the basic reference material kept in the Institute by precision titrimetry, which needs two weighings of both PSR and the basic reference material, by the same apparatus and method²⁾. Therefore, the contaminations may be canceled against each other. The cancellation, however, cannot be realized in our laboratories, because the drying and handling of PSRs are the concern of their user. This source of error becomes more serious in purity measurements performed by the precise coulometric titration⁵⁾, because we weigh out PSR only one time ; the weighed result must be absolute mass, because other weighing is unnecessary. Thus, the PSR should be weighed in conditions with the least contaminants.

Although we can find many publications on the determination of water⁸⁾⁹⁾ and also a monograph on the measurements of the mass of materials¹⁰⁾, they mainly treat the measuring methods and instruments, and are not concerned enough with the contamination of the substances to be weighed.

Generally, PSRs are first pulverized in an agate mortar (grinding process), then taken into a weighing bottle and heated at a definite temperature for several hours in an oven or a furnace (heating process). Then, they are cooled in a desiccator to room temperature (cooling process) and weighed on a suitable balance.

Unfortunately, we find sometimes quite different procedures for heating several PSRs in the literature. The desiccant in the desiccator on cooling process is also discussed without consensus. Introducing recent works on this problem, the present author tries to find here the optimum procedures for drying PSRs.

2. Condition of Water in Primary Standard Reagents

The reagents of this kind are anhydrous crystalline solid of definite composition and rather stable on heating (reagents containing the water of crystallization will be discussed later). According to the classification by Erday¹¹⁾, water in these kind of crystals is present in three forms: i.e. (i) adsorbed water on the surface of crystals, usually removed at 100 - 130°C, (ii) so-called 'decrepitation water', usually presents in holes and cavities in crystals, and removed at 250 - 300°C, (iii) water adsorbed in microscopic or submicroscopic capillaries and channels, which may be removed only by red-heat (about 600°C).

For the water of kind (i), the adsorption phenomenon is not a simple Langmuir's process, but the BET process is predominant. The amounts of water on, for example, single crystals of sodium chloride synthesized from its melt were about $0.5 \mu\text{g}/\text{cm}^2$ after storage in a desiccator¹²⁾; this was one order of magnitude larger than the value calculated by Langmuir's theory. The amounts were also somewhat larger than those on the surfaces of borosilicate glass and stainless steel¹³⁾. Therefore, the hydration of the ions of the first layer on the crystal surface may be considerable for such ionic crystals. The formation of monohydrated sodium chloride was also possible in this case, though the authors could not identify such a crystal.

On the other hand, there are some non-hygroscopic reagents such as arsenic trioxide, benzoic acid, and potassium hydrogen phthalate. The surface of arsenic trioxide adsorbs gaseous molecules in atmosphere, because the reagent floats first on the surface of its dissolving solution. These kinds of reagents belong to the easily dryable group and do not cause serious problems on handling.

In order to remove the water of kinds (ii) and (iii), the reagents should be pulverized by grinding with agate mortar before heating. Grinding is the only method to minimize the water disturbance for the PSRs which decompose at high temperature, and cannot be omitted for PSRs purified by the recrystallization in a solvent.

3. Heating Conditions

3.1. General consideration

Fundamentally, the problem of heating temperature belongs to the equilibrium state of the sample and should be distinguished from the rate process during which the water vapor goes out of the sample phase. However, the low sensitivity of water determination used previously (mainly the measurement of weight loss) makes it difficult to distinguish the processes. Because we must use a large

Table 1. Summary of drying conditions of primary standard reagents

Reagent	Heating temp. (°C)	Heating time (h)	Remarks	Literature
Amidosulfonic acid	60	4	After washing with anhydr. EtOH and Et ₂ O for recrystallized reagent; can be weighed in atmosphere	15) 16)
	Room temp.	>48	In vacuum desiccator	2)
	ditto	>24	ditto	17)
	ditto	4	ditto	15) 16) 18)
Arsenic trioxide	105 - 110	1 - 4	2 h by NBS, 3 - 4 h by JIS	2) 19)-23)
	105	---	Can be weighed in an open vessel	20)
	Room temp.	24	In vacuum desiccator	17) 21) 24)
	ditto	---	Sublimate → store in a desiccator of CaCl ₂	25)
Benzoic acid	Fuse(130-140)	---	Fuse in Pt crucible → pour into Pt dish, then crush with agate mortar; not hygroscopic	26)-31)
	Fuse (<130)	---	In Pt dish, decomposes at higher temp.	28) 29)
	Room temp.	72	In vacuum desiccator	31)
	Fuse(400)	---	In Pt crucible (m.p. 398°)	32) 33)
Potassium dichromate	Fuse then 100 - 110 300	---	Fuse at lowest temp. → cool crush → heat 100 - 110°	34)
		---	40 - 70 ppm of carbon from organic impurities could be detected, indicating decomposition of the reagent	35)
	260	---	Water (0.018 %) was detected at this temp.	36)
	200	---	Fusion is advisable; residual water was 0.01 % at this temp.	33) 37)
	150 - 200	---	Recrystallization → pulverization → heat. Disturbance of organic impurities was neglected below this temp.	35) 38) 39)
	150	---	Heat after pulverization	40)-44)
	140 - 150	>1	ditto	45)
	130	6	ditto, cool in a desiccator of P ₂ O ₅	46)
	110	24	ditto, cool in a desiccator of Mg(ClO ₄) ₂	47) 48)
	100 - 120	>2	ditto	2) 48)-51)

Potassium hydrogen phthalate	125	---	Should be < 135°	26) 29) 52)
	120	1 - 5	Usually after grinding with agate mortar to about 100 mesh	14) 27) 31)
				53) - 58)
	100 - 110	2 - 24	After drying, water content cannot be higher than 0.003 %	17) 29) 48)
				56)
Potassium iodate	180	6	After recrystallization	22) 59) - 63)
	150 - 180	---		64) 65)
	120 - 140	1 - 2		2) 66) 67)
Sodium carbonate	Fuse		Fuse in CO ₂ , gradually change with air on cooling	68)
	500 - 650	40-50(min)	In Pt crucible	2)
	350 - 400	Several h	In Pt dish	53)
	270 - 300	0.5 - 5	Mainly after decompn. of recrystall. NaHCO ₃ , sometimes Pt-ware	69) - 75)
	270 ± 10		After decompn. of NaHCO ₃ in Pt crucible	16) 76)
	260 - 265	30(min)	In Pt crucible, after decomposition of NaHCO ₃ at 120°, decomposes over 270°	77)
	250	---		78)
	140	1		79)
Sodium chloride	820 - 830	10(min)	Fuse in Pt dish after heating at 250 - 300°	80) 81)
	Fuse → 110	---	Fuse in Pt dish → cool, crush → heat at 110°	82)
	500 - 650	40-50(min)	In Pt crucible	2)
	500 - 600	---	Electric furnace is recommendable	83) 84)
	200	2 - 18	Heat after pulverization	85)
	130	18	For fine powder, this temp. was enough	85)
	105 - 120	1 - 2		86)
Sodium oxalate	200 - 250	2 - 3	Decomposition begins at higher than 280°	35)
	240	20	Weight loss was 0.009 %; residual water was 0.02 - 0.03 %	87) 89)
	200	---	Cool in a desiccator of CaCl ₂	88) 89)
	150 - 200	---		2)
	> 150		Not complete at 150°C	89)
	125 - 150	---	Residual water was 0.1 % by 125° heating	89)
	105 - 120	> 2		87) 90) - 94)

amount of sample for the investigation by gravimetry, the temperature of the sample is elevated rather slowly and inhomogeneously. This makes it difficult to remove the last trace of water in the inner part of the sample, and may give rise to false decision of drying at pseudo-constant weight. The particle size of the reagent influences the liberation and the diffusion of the water vapor evolved from the reagent phase especially in the inner part, and also influences the hygroscopicity of the reagent. Therefore, use of extremely fine powder is not recommendable. For example, pulverizing to somewhat under 100 mesh was recommended for potassium hydrogen phthalate¹⁴⁾. The possibility of the thermal decomposition of the reagent should also be considered on the grinding process.

On the other hand, the difficulty of the precise measurements of main constituent in PSR (direct assay) requires the heating temperature to be kept low, because we are usually afraid of the decomposition of the reagent at higher temperature. Various conditions for drying PSRs are therefore described in the literature.

3.2. Heating temperature

The heating temperatures previously recommended in various references are summarized in Table 1 along with some comments.

The data of the table allow us to divide the reagents into three groups; the first group whose conditions are the same as found in the literature includes not so hygroscopic reagents such as amidosulfonic acid, arsenic trioxide, benzoic acid, and potassium hydrogen phthalate; the second group in which temperatures are widely different, as is the case for potassium dichromate and sodium carbonate, and third group, which includes reagents such as sodium chloride, sodium oxalate, etc.

The present author already reviewed the conditions for each reagent^{3,4,95)}. Therefore, he will give here short reviews and discussion on the recent reports on some reagents.

Potassium dichromate --- The reagent is usually purified by recrystallization and contains 'decrepitation water'⁹⁶⁾⁻⁹⁸⁾ in it. Therefore, drying at rather high temperature (300°C for example) may be recommendable. Yoshimori and Sakaguchi⁹⁹⁾ found that the amounts of residual water in the reagent were less than 25 ppm when it was heated at higher than 200°C and cooled in a dessicator without contamination of atmospheric moisture, and that the reagent is stable on heating, because it could be purified by the zone melting method¹⁰⁰⁾. Thus, the present author recommended previously the heating at higher than 250°C⁹⁵⁾. However, he recently found the presence of some organic impurities even in the SRM from NBS. The amounts were found to be about 10 and 30 ppm as carbon for the NBS SRM 136c and the RMs certified by IJLJ respectively by heating them at 300°C³⁵⁾. When the purities of the dried reagents were determined by the precise coulometric titration after heating the samples between 150 and 300°C, they decreased distinctly between 200 and 250°C. Therefore, the decomposition of the reagents by organic impurities occurred within this temperature range, and the drying temperature for this reagents should be 150 - 200°C for usual PSR.

Sodium carbonate --- Although this reagent was recommended as PSR by the Society of Analytical Chemistry⁷⁶⁾ and IUPAC¹⁶⁾, a wide variety of drying procedures for this was found in the literature, some of them were summarized by Laitinen⁶⁸⁾. Previously, warnings were given about the decomposition of the reagent by heating it higher than 270°C^{77,101)}. However, Kolthoff and Stenger¹⁰²⁾ pointed out some inconsistency in the data of Smith and Croad¹⁰¹⁾. Taylor and Smith⁵³⁾ dried this at 380 - 400°C for their coulometric assay and obtained excellent results. Yoshimori and Sakaguchi⁹⁹⁾ indicated that the reagent may be dried nearly completely by heating it at 600°C, and Yoshimori et al.¹⁰³⁾ also found that the dissociation of this (i.e. liberation of carbon dioxide) began not at 800°C but at 820°C on their investigation of the decomposition of sodium oxalate. Therefore, the present author supports the opinion of Newkirk and Aliferis¹⁰⁵⁾, that is, the decomposition of the reagent at rather low temperature may be based on the reaction between the reagent and siliceous materials present as an impurity in it and/or in the container. Therefore, the heating in a porcelain crucible (under stirring, thermometer measurement) which was used in a textbook⁷⁴⁾ cannot be recommended. Thus, this reagent should be heated at least 300°C in a platinumware, using an electric furnace; it should be cooled by placing the platinumware in a weighing bottle (c.f. next section), because some authors¹⁰⁵⁾ warned that the dried reagent adsorbed more than 0.07 % of water during cooling and weighing periods. Sulfuric acid must not be used as the desiccant in the cooling desiccator⁹⁹⁾.

Sodium oxalate --- Since the reaction between this reagent with permanganate is not so simple¹⁰⁶⁾¹⁰⁷⁾, some authors (Kolthoff et al.¹⁰⁸⁾ for example) do not recommend this as the PSR for permanganate solution. However, this is still widely used in many laboratories. The reagent is rather stable on heating and not so hygroscopic⁸⁷⁾¹⁰³⁾¹⁰⁹⁾. The decomposition temperatures in the literature are consistent, being not lower than 250°C. Recently, Yoshimori et al. determined trace amounts of carbon monoxide liberated by heating the reagent at various temperatures, and found that the liberation could not be found at 280°C and nearly 20 ppm of the monoxide could be determined by heating the reagent at 290°C for 3 h¹⁰³⁾. They also showed that the residual water in the reagent after cooling was much less compared with that of sodium carbonate. They recommended, however, the heating at 200 - 250°C, because hygroscopicity of the reagent could be appreciably decreased by such high temperature heating and calcium chloride was enough as the desiccant for the cooling desiccator. For decomposition of the reagent to sodium carbonate, it should be heated between 750° and 800°C, because the decomposition was not complete at lower temperature within 1 h and the liberation of carbon dioxide could be found at 820°C.

4. Apparatuses for Heating

4.1. Sample container

In order to release the moisture from the sample layer more easily, the layer should be as thin as possible. Therefore, a flat weighing bottle of wide bottom area is preferable. The thickness of glass of the bottle also exercises

some influence on the heat capacity and so on the heating time for the drying. The material of the bottle is the next problem. Soft glass is sometimes recommended to remove the disturbance of electrostatic charge on the surface of the bottle¹¹⁰⁾. Such glass, however, liberates an appreciable amount of water by high temperature heating (more than $5 \mu\text{g}/\text{cm}^2$ at 300°C for several hour)¹³⁾. The amounts of such water for borosilicate glass were one order of magnitude less than those of soft glass and only $0.05 \mu\text{g}/\text{cm}^2$ or less for quartz glass. The electrostatic charge of such 'dry' glasses may be removed by plating a very thin film of platinum or gold metal^{111,112)} or by placing a soft radiation source inside the balance case. Metallic aluminum is not recommendable as the container, because it liberates various kinds and so various amounts of water (adsorped and/or combined with surface alumina) according to the temperature of heating¹¹³⁾.

How tightly the ground part of the bottle is kept from atmosphere contact is very important for the PSRs of hygroscopic nature during cooling and weighing periods, and this problem will be discussed later. Introduction of air before weighing is very important to avoid the error due to the reduced pressure inside the bottle after cooling. Thus, the weighing bottle recommended by Hillebrand et al.¹¹⁴⁾ gives us valuable information.

4.2. Heating oven or furnace

A PSR in a weighing bottle or in a platinum crucible is heated in an oven or in a furnace kept at a definite temperature. Here, we should keep in mind that the temperature of the PSR may not be the same as that of the thermometer reading. According to the summary by Mellor and Thompson¹¹⁵⁾, the maximum temperature ranges of an electrically heated and controlled oven whose thermometer indicated 107°C fluctuated between 99 and 114°C at the top shelf and $90 - 108^\circ\text{C}$ at the bottom shelf. Better constancy was obtainable by a gas-heated steam jacket oven, but high temperature heating is difficult by the oven, though about 110°C is obtainable by the use of toluene. Instead of a gravity convection oven, a mechanical convection (by circulation of hot air) oven is more advisable because of the constancy of the temperature (less than several %) and of shortening the heating time. The latter phenomenon will be described in the next section.

An electric furnace is advisable for heating the PSRs at higher temperature ($>300^\circ\text{C}$), because it is easy to control the temperature and to avoid the harmful influence by sulfur oxides which are usually produced on gas-heating.

5. Heating Time

This is the most difficult factor to decide correctly. As shown in section 3.1, the liberation of water from PSR is a rate process of heterogeneous system, and concerned with nearly all conditions and devices. They include: condition of water in the sample, the amount and the nature of the sample, particle size, heat capacity and thermal conductivity of the container, surface area and the thickness of the sample layer, rate of removing the moisture liberated from the sample layer, heating temperature, power of the heating source of the oven or the furnace (heating rate), condition of the use of heating device (common use or exclusive use),

type of the oven (mechanically convected or not; the dimensions), etc.

Of course, it is impossible to keep all of the above conditions constant. Therefore, the direction 'dry the reagent at 100 - 110°C (or other temperature) until a constant weight is obtained' can not be considered as irresponsible. Every analyst should certify how long time is necessary for him to obtain constant weight of the reagent under his own circumstances. The certification is, however, carried out usually by the measurement of weight loss of the sample. Therefore, the present author describes here some examples and precautions which the analyst should remember.

During the investigations on the drying conditions of iron ores¹¹⁶⁾ and bauxites¹¹⁷⁾, the present author heated several centigrams of the samples in a quartz boat with a small furnace in which the inner diameter of the heating tube was about 25 mm. He found that the previously heated and cooled samples liberated their residual water about 20 min after the second introduction into the heated furnace. This indicated that nearly 20 min was necessary for the sample and the boat to get to the temperature of the furnace. Thus, it may be considerable for safety that the sample in a weighing bottle arrives at the temperature of the oven about 30 min after its introduction into the oven. More serious influence may be caused by the use of a cold saucer (for example cold watch glass) and by opening the door of an oven in common use. Heating for 1 h is advisable to certify the constant weight of the sample; otherwise we may get the false (pseudo) constant weight.

A drying oven heated with hot air circulation (mechanically convected) is highly recommendable, because the circulation enables us to decrease the temperature fluctuation and to heat the cold sample more quickly; also, the water vapor liberated from the PSR may be removed very rapidly. Therefore, the heating time may be shortened appreciably. For example, Willits¹¹⁸⁾ stated in his excellent discussion "drying is usually about four times as fast in mechanically convection ovens as in gravity convection ovens", and also "actually, with the use of pre-desiccated air, an air oven would be as effective as a vacuum oven". Harris⁸⁾ also stated the same opinion.

Heating in a 'hot tube' under the stream of dried air or in an apparatus like Abderhalden's may be very effective for the dehydration of a sample. However, the effectiveness of the heating process does not guarantee that the sample will be kept in such dried condition during its cooling and weighing processes. These problems will be discussed in the following section.

6. Cooling and Weighing

After heating, PSRs should be cooled in a desiccator containing a suitable desiccant. Big differences in the drying ability of desiccants could be found in the literature; some are summarized in Table 2¹¹⁹⁾. Some analysts hope to use more powerful desiccant in his desiccator. However, the power is important only for the dehydration of a sample at room temperature by the storage for a long time. We must not forget that dry air is heavier than moist air. For example, Booth and McIntyre¹²⁵⁾ showed that the atmosphere in a desiccator arrived at the equilibrium

Table 2 Comparison of power of several desiccants¹¹⁹⁾

Reagent	Residual water in dehydrated gas (μg/l)			
	Bower ¹²⁰⁾ (30.5°)	I.C.T. ¹²¹⁾ (25°)	T.&D. ¹²²⁾ (25°)	Others [*]
Liq.N ₂ (-190°)	---	1.6x10 ⁻²⁰	---	10 ⁻¹³ (E)
Dry-ice + EtOH	---	---	---	10 ⁻⁶ (E)
P ₂ O ₅	(Std.)	< 0.02	< 3.6	---
Molecular sieve 5A	---	---	3.9	0.1 (H)
Mg(ClO ₄) ₂	2	< 0.5	< 1.5	---
BaO	0.65	---	2.8	---
Mg(ClO ₄) ₂ ·3H ₂ O	30	< 2	---	---
KOH(fused)**	---	2	939	14 (H)
Al ₂ O ₃ (gel)**	5	3	2.9	6 (H)
CaO**	3	200	656	---
H ₂ SO ₄ (98.5%)**	---	3	---	---
CaSO ₄ **	5	---	67	4 (H)
SiO ₂ (gel)***	30	---	70	200-300(E) or 500
CaCl ₂ (gran.)	1500	140-250	67	---
NaOH(fused)	---	160	93	---
CaCl ₂ (anhydr. or fused)	360	360	137	200 (H)
H ₂ SO ₄ (95%)**	---	300	---	---

* E : ref.123 , H : ref.124

** Not recommended by inconsistent results, less capacity of acid liberation

*** Blue gel turns pink after the vapor pressure of water increased over 1.5 mm Hg which is the pressure of hydrated cobalt (II) chloride.

state only about 2 h after closing the lid, and Belcher and Mott¹²⁶⁾ indicated the inefficiency of a desiccator in determining the moisture in coal. Thus, Strouts et al.¹²⁷⁾ stated that the desiccant in the desiccator for cooling the heated materials was useless. According to the study of Yoshimori and Sakaguchi⁹⁹⁾, no appreciable difference could be found between magnesium perchlorate and concentrated sulfuric acid for cooling potassium dichromate, but the latter should not be used for sodium carbonate. Yoshimori et al.¹⁰³⁾ also indicated by using sodium oxalate that the difference in the power between magnesium perchlorate and calcium chloride could be found when the heating temperature was lower than 150°C. The difference was less than 30 ppm of residual water by heating at 100°C, but the difference decreased to less than 10 ppm by heating the oxalate at higher than 200°C. They concluded that the heating temperature is more important than the choice of the desiccant in the desiccator on cooling the heated samples.

The next precaution on the use of a desiccator concerns the number of the samples in it. According to the experience of the present author, when he heated two weighing bottles containing potassium dichromate for drying, cooled in one desiccator and assayed them in order by the precise coulometric titration, the result (purity) obtained for the latter portion was more than 0.1 % lower compared with that for the former. This indicated that the latter had been contaminated by atmospheric moisture which entered into the desiccator by the previous opening of the lid. Therefore, only one sample should be cooled in one desiccator, and subdivision of a large amount of a sample after drying should be avoided even though the sample was stored in a desiccator. The desiccator shown by Peck in U.S. Geological Survey¹²⁸⁾ is satisfactory to avoid these troubles. That was the combination of four small desiccators in one block and each desiccator could contain only one sample (crucible) in it.

On weighing a sample, the use of a counterpoise and a double-pan balance is advisable to decrease the error due to the fluctuation of the surface condition of the weighing bottle. The counterpoise consisted of an empty bottle of the same shape and material, nearly the same weight (but slightly lighter) and treated by the same process as the sample container, and placed on the right-hand pan of the balance together with weights. As an example of the effectiveness of this technique, nickel in a nickel-base heat resistant alloy was determined by the gravimetry with dimethylglyoxime¹²⁹⁾. The sintered-glass filter crucible which had nearly the same weight but was somewhat lighter than that containing the glyoximate precipitate was used as the counterpoise. All treatments and handlings of the crucible were carried out in parallel with that containing the precipitate, which was placed on the right-hand pan with weights. The precisions of the results were usually 0.1 % or less as the relative standard deviation, and indicated that the influences by the hygroscopicity and erosion by the solutions of the sintered-glass frit¹³⁰⁾ could be nearly removed by this procedure.

7. The Reagents Containing Water of Crystallization and the Use of Single Crystals.

Sodium tetraborate (Borax) and oxalic acid have been used as PSRs, and their conditionings were shown in the literature²⁶⁾¹³¹⁾⁻¹³⁴⁾. Usually, they were stored in a hygrostat after recrystallization and/or dehydration for more than 3 months under frequent stirring. The saturated solution of sodium bromide (R.H. 57 % at 25°C, 59 % at 20°C) was usually used in the hygrostat, and that of the mixture of sodium chloride and sucrose was also used for the tetraborate¹³⁵⁾. Kolthoff et al.¹³³⁾ highly recommended the borate as the PSR.

Recently, Tanaka and Yoshimori¹³⁶⁾ investigated the purity of disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA salt) by the precise coulometric titration, and used the reagent and the method for the precise determination of aluminum. They stored two reagents, commercially obtained and once dehydrated at 120°C in vacuo, in the hygrometers containing saturated sodium bromide solution. The fluctuations of the purities of the reagents were 0.009 % after 6 months for the former and only 0.002 % after 15 months for the latter (each as

the relative standard deviation). Therefore, hydrated salts are also useful as PSRs if enough conditionings are given.

More than 100 years ago, the crystal of "Iceland Spar" was recommended as the PSR of acidimetry¹³⁷⁾. Unfortunately, the present author has not seen the crystal yet. Practical use of the single crystals was rather recently tried by Bates and Wichers¹³⁸⁾. They prepared single crystals of benzoic acid and measured the purity of potassium hydrogen phthalate and oxalic acid dihydrate by using the crystals as the standard. More recently, the use of some single crystals was tried in the author's laboratory. Some single crystals of sodium chloride which obtained from a broken cell for infra-red spectroscopy was assayed by the precise coulometric titration¹²⁾. The purities of the crystals were usually higher than 99.99 %, and enough to use as the PSR, though the assay results somewhat fluctuated (less than 0.015 % as the standard deviation). Some large (> 5 g, perhaps single) crystals of amidosulfonic acid prepared by evaporation of its solution in a thermostat¹³⁹⁾ and arsenic trioxide small single crystals prepared by sublimation in vacuo¹⁴⁰⁾ were also assayed by the same method as above. Mean purities of them were higher than 99.95 % for the former and 100.003 ± 0.009 % for the latter. Surface water of these crystals was usually less than 0.003 %, and they may be used without any drying. The method of zone-melting was also applied by Yoshimori et al.¹⁰⁰⁾ for the purification of potassium dichromate. They obtained the aggregates of crystals of the reagent, and assayed them. The purities of the reagents obtained by more than three passages of the molten zone were higher than 99.99 %, and the amounts of water in the aggregates were less than 0.002 %. All results shown above indicated that these crystals may be useful as PSR without special treatments for drying, though their purities are usually somewhat less than 100 %. The differences, however, were very small except amidosulfonic acid, and indicated that the use of these crystals was practically advisable to improve the 'measurement compatibility' of titrimetric analyses between many laboratories.

8. Conclusion

As the conclusion of this review, the temperatures shown in Table 3 are recommended for heating the PSRs. On the other hand, the author cannot give the valuable conclusion for heating time, owing to the reasons described in section 5. Generally speaking, however, the heating about 3 h is perhaps enough to decrease the error based on the water in PSR to less than 0.1 % by using an ordinary gravity convection oven which is electrically heated and controlled and without opening the door during the heating period. More than 1 h of heating is necessary for the PSR to certify that a constant weight is obtained. Of course, the PSR should be placed near the thermometer in the oven. As the desiccant in the cooling desiccator, magnesium perchlorate is most satisfactory for the hygroscopic (2nd group in Section 3.2) reagents. Calcium chloride, however, is enough for the other reagents. Rather than the selection of the desiccant, we must weigh the heated reagent as fast as possible after cooling in the desiccator.

Table 3 Recommendable Heating Temperatures for Drying PSRs

Reagent	Temperature (°C) and remarks*
Amidosulfonic acid	Room temp., in vacuum desiccator for more than 48 h
Arsenic trioxide	100 - 110°
Benzoic acid	Fuse (130°) in a Pt crucible, pour into Pt dish, then crush; or room temp., in vacuum desiccator for 72 h.
Potassium dichromate	150 - 200°, after pulverizing
Potassium hydrogen phthalate	110 - 120°, after pulverizing about 100 mesh
Potassium iodate	180°
Sodium chloride	500 - 650°, in a Pt crucible, an electric furnace should be used; > 300° may be used
Sodium oxalate	200 - 250°; 150° may be used

* Formerly written conditions are more advisable.

If an analyst hopes to decrease the error of his titrimetry to less than 0.1 %, nearly all precautions described in this review should be considered. Any omissions may give serious error to the results. Accurate results require much cost, time and tenacity of purpose.

References

- 1) G. A. Uriano : CRC Crit. Rev. Anal. Chem., 6, 361 (1977).
- 2) JIS (Japanese Industrial Standards), K 8005 1966.
- 3) T. Yoshimori, T. Tanaka : Bunseki Kagaku, 22, 1251 (1973).
- 4) T. Yoshimori : Talanta, 22, 827 (1975).
- 5) T. Yoshimori : Z. Chem. (Leipzig), 18, 251 (1978).
- 6) P. S. Tutundzic : Anal. Chim. Acta, 8, 182 (1953).
- 7) Commission on Electroanalytical Chemistry, Analytical Chemistry Division of IUPAC, Information Bulletin of Appendices on Provisional Nomenclature Symbols, Units, and Standards, No.35, Aug. 1974.
- 8) C. Harris : Talanta, 19, 1523 (1972).
- 9) J. Mitchell, Jr., D. M. Smith : "Aquametry", 2nd Ed., part I (1977), part III (1980), (John Wiley, New York).
- 10) K. Yamamoto (editor) : "Shitsuryô no Seimitsu-sokutei Manual", Nihon Kikaku Kyokai (1981).
- 11) L. Erdey : "Gravimetric Analysis", Part I, p. 298 (1963), (Macmillan, New York).

- 12) T. Yoshimori, T. Tanaka : Anal. Chim. Acta, 55, 185 (1971).
- 13) T. Yoshimori, S. Ishiwari, Y. Watanabe, T. Harada, S. Yamada : Trans. Japan Inst. Metals, 14, 396 (1973); Nippon Kinzoku Gakkai Shi, 35, 808 (1971).
- 14) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : "Applied Inorganic Analysis", 2nd Ed., p.180 (1953), (John Wiley, New York).
- 15) Analytical Methods Committee : Analyst (London), 92, 587 (1967).
- 16) Commission on Analytical Nomenclature, Analytical Chemistry Division of IUPAC : Pure Appl. Chem., 18, 445 (1969).
- 17) T. Katoh : Bunseki Kagaku, 2, 402 (1953).
- 18) R. Belcher, A. J. Nutten, A. M. G. MacDonald : "Quantitative Inorganic Analysis", 3rd Ed., p.161 (1970), (Butterworths, London).
- 19) K. M. Sappenfield, G. Marinenko, J. L. Hague : Natl. Bur. Stds., Spec. Publ., 260-24, p.4 (1972).
- 20) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : p.188, 199 in Ref. 14.
- 21) R. J. Winterson (edited by C. L. Wilson, D. W. Wilson) : "Comprehensive Analytical Chemistry", vol. IB, p.240, 246 (1960), (Elsevier, Amsterdam).
- 22) S. M. Tuthill, R. S. Sprague, W. C. Stoecker : Anal. Chem., 36, 1994 (1964).
- 23) C. R. N. Strouts, H. N. Wilson, R. T. Parry-Jones, (editors) : "Chemical Analysis, The Working Tools", 2nd Ed., Section 9.4.1.C. (1962), (Clarendon, Oxford).
- 24) I. M. Kolthoff, R. Belcher : "Volumetric Analysis", vol. III, p.41 (1957), (Intersci., New York).
- 25) F. P. Treadwell, W. T. Hall : "Analytical Chemistry", 9th Ed., vol. II, p.591 (1942) (Wiley, New York).
- 26) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : "Quantitative Chemical Analysis", 4th Ed., p.783 (1969), (Macmillan, London).
- 27) H. A. Laitinen : "Chemical Analysis", p.92 (1960), (McGraw-Hill, New York).
- 28) W. F. Hillebrand, G. E. Lundell, H. A. Bright, J. I. Hoffman : p.181 in Ref. 14.
- 29) I. M. Kolthoff, V. A. Stenger : "Volumetric Analysis", 2nd Ed., vol. II, p.94 (1947), (Intersci., New York).
- 30) E. R. Weaver : J. Am. Chem. Soc., 35, 1309 (1913).
- 31) T. Yoshimori, I. Matsubara : Bull. Chem. Soc. Jpn., 43, 2800 (1970).
- 32) J. W. Mellor, H. V. Thompson : "A Treatise on Quantitative Inorganic Analysis", 2nd Ed., p.501 (1938), (Charles Griffin, London).
- 33) I. M. Kolthoff, R. Belcher : p.176 in Ref. 24.
- 34) N. H. Furman (editor) : "Scott's Standard Methods of Chemical Analysis", 6th Ed., Vol. I, p.1334 (1962), (Van Nostland, Princeton).
- 35) T. Yoshimori, K. Kamijoh : Talanta, 29, 343 (1982).
- 36) K. M. Sappenfield, G. Marinenko, J. L. Hague : p.26 in Ref. 19.
- 37) C. Woodward, H. N. Redman : "High-precision Titrimetry", p.36 (1973), (The Soc. for Anal. Chem., London).
- 38) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.839 in Ref. 26.
- 39) R. Belcher, A. J. Nutten, A. M. C. MacDonald : p.233 in Ref. 18.
- 40) J. Grant : "Sutton's Volumetric Analysis, A Systematic Handbook of Volumetric Analysis", 13th Ed., p.193 (1955), (Butterworths, London).
- 41) G. G. Rao : Talanta, 13, 1473 (1966).
- 42) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : p.189 in Ref. 14.
- 43) R. J. Winterson : p.242 in Ref. 21.

- 44) C. R. N. Strouts, H. N. Wilson, R. T. Parry-Jones (editors) : Section 9.6.2.f, in Ref. 23.
- 45) R. G. Monk, G. C. Goode: Talanta, 10, 51 (1963).
- 46) G. Marinenko : NBS Technical Note 543, p.47 (1970).
- 47) G. Marinenko, J. K. Taylor : J. Res. Natl. Bur. Stds., 67A, 453 (1963).
- 48) J. Knoeck, H. Diehl : Talanta, 16, 181, 567 (1969).
- 49) T. Yoshimori, I. Matsubara, K. Hirose, T. Tanaka : Bunseki Kagaku, 19, 681 (1970).
- 50) K. M. Sappenfield, G. Marinenko, J. L. Hague : p.39 in Ref. 19.
- 51) E. H. Archibald : "The Preparation of Pure Inorganic Substances", p.281 (1932) (Wiley, New York).
- 52) E. R. Caley, R. H. Brundin : Anal. Chem., 25, 142 (1953).
- 53) J. K. Taylor, S. W. Smith : J. Res. Natl. Bur. Stds., 63A, 153 (1959).
- 54) E. L. Eckfelt, E. W. Schaffer, Jr. : Anal. Chem., 37, 1534 (1965).
- 55) T. Yoshimori, I. Hikawa : Bunseki Kagaku, 16, 927 (1967).
- 56) J. Grant : p.114 in Ref. 40.
- 57) R. Belcher, A. J. Nutten, A. M. G. MacDonald : p.287 in Ref. 18.
- 58) H. H. Willard, N. H. Furman, C. E. Bricker : "Elements of Quantitative Analysis", 4th Ed., p.143 (1956), (Van Nostrand, N. J.).
- 59) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.819 in Ref. 18.
- 60) R. J. Winterson : p.252 in Ref. 21.
- 61) N. H. Furman : p.1336 in Ref. 34.
- 62) R. Belcher, A. J. Nutten, A. M. G. MacDonald : p.243 in Ref. 18.
- 63) H. A. Laitinen : p.398 in Ref. 27.
- 64) I. M. Kolthoff, V. A. Stenger : p.88 in Ref. 29.
- 65) I. M. Kolthoff, R. Belcher : p.92 in Ref. 24.
- 66) R. J. Winterson : p.273 in Ref. 21.
- 67) R. Belcher, A. J. Nutten, A. M. G. MacDonald : p.253 in Ref. 18.
- 68) H. A. Laitinen : p.86 in Ref. 27.
- 69) F. A. Cooper, J. C. Quayle : Analyst(London), 91, 365 (1966).
- 70) R. J. Winterson : p.213 in Ref. 21.
- 71) I. M. Kolthoff, V. A. Stenger : p.80 in Ref. 29.
- 72) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.778 in Ref. 26.
- 73) R. Belcher, A. J. Nutten, A. M. G. MacDonald : p.160 in Ref. 18.
- 74) F. P. Treadwell, W. T. Hall : p.481 in Ref. 25.
- 75) J. Grant : p.107 in Ref. 40.
- 76) Analytical Methods Committee : Analyst(London), 90, 251 (1965).
- 77) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : p.176 in Ref. 14.
- 78) E. W. Balis, L. B. Bronk, H. A. Liebhafsky, H. G. Pfeiffer : Anal. Chem., 27, 1173 (1955).
- 79) W. A. Carmody : Ind. Eng. Chem., Anal. Ed., 17, 577 (1945).
- 80) R. J. Winterson : p.231 in Ref. 21.
- 81) N. H. Furman : p.1340 in Ref. 34.
- 82) G. Marinenko, J. K. Taylor : J. Res. Natl. Bur. Stds., 67A, 31 (1963).
- 83) I. M. Kolthoff, V. A. Stenger : p.251 in Ref. 29.
- 84) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.795 in Ref. 26.

- 85) G. Marinenko, C. E. Champion, (edited by J. K. Taylor) : NBS Technical Note 505, p.65 (1969).
- 86) R. Belcher, A. J. Nutten, A. M. G. MacDonald : p.187 in Ref. 18.
- 87) K. M. Sappenfield, G. Marinenko, J. L. Hague : p.54, 60 in Ref. 19.
- 88) J. W. Mellor, H. V. Thompson : p.175 in Ref. 32.
- 89) I. M. Kolthoff, V. A. Stenger : p.40 in Ref. 29.
- 90) F. P. Treadwell, W. T. Hall : p.538 in Ref. 25.
- 91) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : p.187 in Ref. 14.
- 92) N. H. Furman : p.1337 in Ref. 34.
- 93) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.825 in Ref. 26.
- 94) I. M. Kolthoff, R. Belcher : p.52 in Ref. 24.
- 95) T. Yoshimori : Z. Chem. (Leipzig), 18, 211 (1978).
- 96) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.194 in Ref. 26.
- 97) F. W. Schwab, E. Wichers : J. Res. Natl. Bur. Stds., 33, 121 (1944).
- 98) H. Diehl : private communication.
- 99) T. Yoshimori, N. Sakaguchi : Talanta, 22, 233 (1975).
- 100) T. Yoshimori, T. Tanaka, M. Ogawa, T. Horikoshi : Anal. Chim. Acta, 63, 351 (1973).
- 101) G. F. Smith, G. F. Croad : Ind. Eng. Chem., Anal. Ed., 9, 141 (1937).
- 102) I. M. Kolthoff, V. A. Stenger : p.81 in Ref. 29.
- 103) T. Yoshimori, Y. Asano, Y. Toriumi, T. Shiota : Talanta, 25, 603 (1978).
- 104) A. E. Newkirk, I. Aliferis : Anal. Chem., 30, 982 (1958).
- 105) I. M. Kolthoff, V. A. Stenger : p.83 in Ref. 29.
- 106) I. M. Kolthoff, R. Belcher : p.48 in Ref. 24.
- 107) R. M. Fowler, H. A. Bright : J. Res. Natl. Bur. Stds., 15, 493 (1935).
- 108) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.827 in Ref. 26.
- 109) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : p.186 in Ref. 14.
- 110) I. P. Alimarin, B. I. Frid : "Quantitative mikro-chemische Analyse der Mineralien und Erze", p.14 (1965), (Verl. Theodor Steinkopff, Dresden).
- 111) I. Fujishima, T. Takeuchi : Bunseki Kagaku, 10, 747 (1961).
- 112) F. A. Cooper, J. C. Quayle : Analyst(London), 91, 363 (1966).
- 113) T. Yoshimori, S. Usuki : Summary of the Lecture for the 43rd Meeting for Anal. Chem., p.413 (1982), (Japan Soc. Anal. Chem.).
- 114) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : p.26 in Ref. 14.
- 115) J. W. Mellor, H. V. Thompson, p.135 in Ref. 32.
- 116) T. Yoshimori, Y. Asano, T. Harada : Talanta, 25, 169 (1978).
- 117) T. Yoshimori, Y. Asano, Y. Hattori : Talanta, 26, 527 (1979).
- 118) C. O. Willits : Anal. Chem., 23, 1058 (1951).
- 119) Japan Soc. Anal. Chem., (Editor in Chief : H. Hamaguchi) : "Bunseki Kagaku Handbook", 3rd Ed., p.1329 (1981) (Maruzen, Tokyo).
- 120) J. H. Bower : U. S. Bur. Std. J. Res., 12, 231 (1934).
- 121) E. W. Washburn (editor) : "International Critical Tables", vol. III, p.385 (1928) (McCraw-Hill).
- 122) F. Trusell, H. Diehl : Anal. Chem., 35, 674 (1963).

- 123) L. Erdey : p.295 in Ref. 11.
- 124) N. Hara : Kôbunshi, 10, 565 (1961).
- 125) H. S. Booth, L. McIntyre : Ind. Eng. Chem., Anal. Ed., 8, 148 (1936).
- 126) R. Belcher, R. A. Mott : J. Appl. Chem., 1, 204 (1951).
- 127) C. R. N. Strouts, H. N. Wilson, R. T. Parry-Jones (editors) : Section 4.3.8b. in Ref. 23.
- 128) L. C. Peck : U. S. Geol. Survey Bulletin, 1170, p.10 (1964).
- 129) T. Yoshimori, Y. Mori, S. Sakai : Summary of the Lecture to the 22nd Annual Meeting of the Japan Soc. Anal. Chem., 1C19, p.B-263 (1973).
- 130) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.468 in Ref. 26.
- 131) N. Schoorl : Chem. Weekblad, 25, 73, 534 (1928).
- 132) I. M. Kolthoff, V. A. Stenger : p.86 in Ref. 29.
- 133) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein : p.779 in Ref. 26.
- 134) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman : p.178 in Ref. 14.
- 135) H. Menzel : Z. Anorg. Allg. Chem., 224, 10 (1935).
- 136) T. Tanaka, T. Yoshimori : Bull. Chem. Soc. Jpn., 53, 661 (1980).
- 137) J. W. Mellor, H. V. Thompson : p.38 in Ref. 32.
- 138) R. G. Bates, E. Wichers : J. Res. Natl. Bur. Stds., 59, 9 (1957).
- 139) T. Yoshimori, T. Tanaka : Anal. Chim. Acta, 66, 85 (1973).
- 140) S. Saito, T. Tanaka, T. Yoshimori : Bunseki Kagaku, 22, 1460 (1973).

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