



Validation of Modification of Volumetric Methode of Determination of Sn (Tin) Concentration on Tin Concentrates

Validasi Modifikasi Metode Volumetrik Penentuan Konsentrasi Sn (Timah) Pada Konsentrat Timah

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ABSTRACT

The analysis techniques for determining the concentration of Stannum (Sn) in Tin Concentrate has been developing since the 19th century. Various methods and analysis techniques are to find the most effective and efficient method enabling to achieve optimal results. The ultimate aims of the research are to generate measurable and testable validation data of modification methods of Tin concentrate analysis. In this study, a modification of the classic volumetric method (SNI 13-6348-2000) that has been used includes modifications to the use of materials and tools in the analysis. In this study, validation of the modified method was also carried out by determining the value of the parameters of Precision, Accuracy, Method of Detection Limit (MDL) and the Ruggedness and Robustness of the method and comparing the acceptability value based on the existing provisions. on the EURACHEM guide. After performing 25 tests using the NCS DC 35002 Certified Reference Material, it was revealed the value of the parameters for the Precision/Relative Standard Deviation (RSD) to be 0.21% (<0.5 CV Horwitz), the accuracy value is 99.9% with bias 0.06%, the MDL values for Minimum Detection Limit (MDL) and Limit of Quantification (LOQ) are 0.4% and 1.32%, respectively. The value of the ruggedness and robustness of the method was carried out by testing in different times and by different analysts and obtained RSD 0.22% (<2/3 CV Horwitz). From the values of the parameters obtained, it can be concluded that the modification of this method fulfills the acceptance value required by EURACHEM.

Keywords: Tin Concentrate, Volumetric, Validation, Stannum (Sn), Iodometric

INTRODUCTION

The development of chemical analysis in determining the Sn content of ore material has been performed for a long time. In April 1931, Marshall. BM in his thesis entitled The Extraction of Tin From its Ore and The Preparation and Behavior of Certain Pure Salt of Tin discussed two main methods in the analysis of determining the amount of Tin in Ore, namely the Reduction and Salification method

(Marshall, 1931). In addition, JW Price in his journal Tin Chemicals in 1978 introduced various analysis techniques with various combinations of compounds such as Tin (IV) Chloride, Tin (II) Sulphate, Tin (II) Fluoroborate, Tin (II) Octoate and others (Price *et. al*, 1978).

From the Norfolk Navy Yard Chemical Laboratory Portsmouth Virginia USA have detailed the reduction technique in determining the TIN concentration through modified

idiometric methods including reagents and sample preparation (Thomas *et. al*, 1944). Wyss, Way-Sui, Yim from the university of London in August 1974 in one chapter of his thesis discussed the problem of determining Tin concentration from geochemical aspects, various ore matrices, sample preparation and homogeneity as well as introducing other alternatives in determining low Sn levels by using Atomic Absorption Spectrophotometer (AAS) instrumentation aid (Wyss *et. al*, 1974). There are at least two journals that describe quite fundamentally and are based on fairly good scientific analysis, namely the first journal published by The Australasian Institute of Mining and Metallurgy in 2017 written by RJ Morgan with the title Estimation of Tin In an Ore in 1927, and the second one is published by the Mining Journal London written by (Parry ARSM, 1923). The two journals discuss the most popular reduction method in the analysis of determining the high concentration of Tin with a comparison of the use of various reducing agents such as Zn (Zinc), Fe (Ferro), and Sb (Antimony) and the influence of several techniques and stages on the possibility of getting errors and weaknesses (Morgan, 1927).

In this study, the authors tried to modify the classic method of analysis of tin concentration in ore commonly used, the iodometric titration reduction method. The modification includes two things, namely modification of tools (crucible, installation of NaHCO_3) and materials (Zn, NaCl, Fe). This modification aims to simplify the analysis process, shorten the analysis time, and most importantly to increase, the value of measurement accuracy and precision. In addition, this modification of the Tin concentration analysis technique is also designed to be able to analyze the tin content from low to high levels with a scale range between 3% to 70% of the TIN content. This method modification will also be statistically validated to see the performance and acceptability of the analysis results.

MATERIAL AND METHODE

Sample

In this study the sample used to validate the modification of this method is Certified Refence Material (CRM) which is a general form of Tin Ore Concentrate with the material code NCS DC 35002 produced by the China National Analysis Center for Iron and Steel in Beijing China. The test was carried out twenty-five times, after

which the data were processed statistically, and the validation parameters were determined.

Process Stages

The determination of Tin concentration through the Iodometric Titration Reduction method is generally divided into at least three important stages, the first is the Decomposition process where the general form of Tin compounds in nature such as the form of Casiterite Oxide (SnO_2) is reduced using Carbon, Hydrogen, Illumination Gas, zinc or potassium cyanide. Reduction using carbon or hydrogen is generally performed at high temperatures in a muffle furnace of about 750 °C with a crucible container. This disintegration process is very important and has been introduced for a long time in the Pearce-Low Method which aims to separate Tin from its associated materials. This disintegration process also determines the level of recovery in the analysis results. Common mistakes that occur in this process are weighing errors and material contamination (Parry, 1923).

The second stage is dissolving, melted Tin is dissolved in strong acid by heating it on a hotplate. Generally, 1: 1 HCl (hydrochloric acid) is used as a solvent, the dissolution product is Stannous Chloride (SnCl_2). The solution was placed in a 300 ml Erlenmeyer, heated and isolated from the outside using CO_2 . Contact of the solution with outside air or oxygen (O_2) will directly change stannous chloride (SnCl_2) to Stannic Chloride (SnCl_4) which has fatal consequences in the analysis results (Sezgin, 2013). Generally, some analysts engineer Sodium Hydrogen Carbonate (NaHCO_3) liquid installation systems, to prevent the solution from coming into contact with the outside air to the cooling and titration process (Gostishchev *et. al*, 2015). The third stage is titration, this process is the last process using 0.01 N to 0.1 N standard solution of Iodine. The solution is usually placed in a manual glass burette, digital burette or automatic titrator. Isolation of the solution from the outside air is continuously carried out during the titration process, this is only possible if the addition of Calcium Carbonate (CaCO_3) granules to the solution during the titration. The choice of the concentration value of the Iodine solution will determine the level of analysis error. The analyst should consider the range of Tin levels to be analyzed with the volume value of the Iodine solution that might be used (Hadi *et.al*, 2018).

Tool Modification

Crucible Modification

RJ Morgan, 1927 in his journal entitled Estimation of Tin in an Ore has suggested an indication of the weakness of the classical method in the analysis of tin concentration determination in the first stage, namely the disintegration stage. When the sample has been heated at 750 °C and reaches its melting point, the sample must be transferred to the dissolving glass container through the crucible washing process. The material inside the crucible is slowly removed from the crucible with a mixture of warm water and acidic liquid with the target that all material can be removed, but with a minimum volume of liquid used (Morgan, 1927). The crucibles used in this process are generally made of iron, zirconium or porcelain with a size of 1.5 inch - 2 inch Figure 1a. Errors are likely to happen when washing is not carried out optimally, so there is still material left on the crucible. The nature of the melt which is easily sticky in other materials such as iron and porcelain makes the washing process longer and ineffective. For this reason, this study is to solve the problem by replacing the typical 3inch crucible with a disposable porcelain crucible with a volume of 8 ml Figure 1b, an upper diameter of 22.5 mm, a height of 29.5 mm and a lower diameter of 16 mm. The type of elemental content in porcelain has been analyzed and the concentration measured to prevent possible contamination during analysis Table 1.



Figure 1. a. Classical 2 inch crucible b. Modified 8 ml crucible

The purpose of this modification is to avoid the process of washing or manually moving the material from the crucible to the Erlenmeyer. With this smaller crucible size, it is possible to put it directly into the Erlenmeyer after the high

temperature heating process without the risky washing process.

With these dimensions and sizes, it is possible to directly include the crucible or melting pot in the process of dissolving in a 300 ml Erlenmeyer without transferring the melt Figure 2b. Beside preventing spills and remaining material, this method can also prevent the addition of excessive liquid to the acid solvent (Hydrochloro Acid) which in turn will reduce the liquid waste generated in the analysis. Mechanically, the presence of a melting pot can help the dissolving process.

Table 1. Material content of Crucible

Element	Concentration (%)
SiO ₂	69.43
Al ₂ O ₃	20.55
Fe ₂ O ₃	0.24
TiO ₂	Nd
CaO	0.08
MgO	0.32
K ₂ O	3.44
Na ₂ O	5.49

Modification of Sodium Hydrogen Carbonate (NaHCO₃) installation

Parry, 1923 in his journal The Assay of Tin and Antimony and RJ Morgan in his journal entitled Estimation of Tin In An Ore also emphasize the importance of isolating the system from outside air, especially oxygen against stannous chloride solutions (SnCl₂) until the iodine titration process is complete and reaches the end point (L Parry et al, 1923). For this reason, several analysts made Sodium Hydrogen Carbonate installations with various techniques. Thomas, 1944 in their journal Determination of Tin By Modified Iodometric Method, have made solution of 10% of NaHCO₃ with a mechanism as shown in Figure 2a. This method is widely used in several TIN analysis laboratories, solutions Sodium Hydrogen Carbonate is flowed through a small pipe through the rubber cover to Erlenmeyer, heating from the solution can still come out without being followed by the entry of outside air in the presence of NaHCO₃ which reacts with HCl to form CO₂ (Thomas *et. al*, 1944). This technique is static and permanent, Erlenmeyer displacement, including stirring and cooling, is rather difficult to do with limited space for movement in the presence of NaHCO₃ installation. In this study, the authors also tried to replace the installation of Sodium Hydrogen Carbonate with U-funnel glass which aims to

make Erlenmeyer more flexible and easy to move. U-Funnel Glass is basically a modification of the funnel glass separator by adding a U shape to the output pipe and installing it on a rubber cap (Stoper Rubber) which aims to be a medium for circulating steam from inside the

Erlenmeyer and simultaneously NaHCO₃ liquid. NaHCO₃ solution will be placed in a U-funnel glass measuring 100 ml as can be seen in Figure 2b.

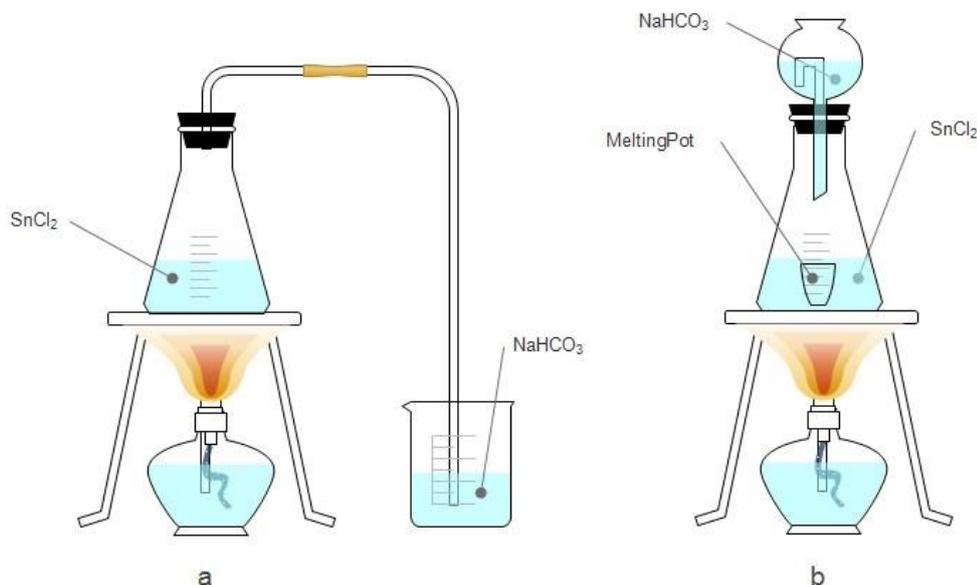


Figure 2. a. NaHCO₃ installation in Classical Methode b. NaHCO₃ installation in Modification Methode

Modification of the use of Material

Zinc Powder (Zn) and Sodium Chloride (NaCl) in the Fusion or Decomposition Process

In the chapter on Alternative Determination Methods written by (Morgan, 1927) it has been explained that the use of Zinc has first been introduced by (JJ Brringer,1925) in his journal in the London Mining Journal which has proved that the use of zinc metal with the combination of sodium hydroxide gives more efficient results in the tin ore reduction process at the fusion or decomposition stage . For this reason, the authors strongly recommend additional zinc with a content of 65.39 grams / mol, min 95 % purity MERCK, Germany and a maximum powder size of 45 micrometers (µm) in the tin ore fusion process before the acid dissolving process in order to obtain maximum recovery. Zinc is actually a sign that there is tin oxide which is not completely reduced by Sodiumhirdoxide so that it can be completely resolved by the presence of zinc according to the reaction:

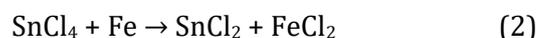


The problem arises when a mixture of sodium hydroxide (NaOH) and zinc (Zn) is placed at a high temperature of about 750 °C,

which is the formation of a melt (liquid) which tends to burst and push the material out of the crucible. This of course will cause the possibility of the sample coming out of the crucible and a negative error in the analysis. Thus, in this study NaCl (Sodium Chloride, 99,99 % purity Merck, Germany) was chosen to overcome this problem since it is a good heat transfer (Heat Capacity) and Sodium Chloride can reach high temperatures (> 700 °C). Sodium Chloride will withstand and prevent direct contact with the material by forming a strong crystal wall without reducing the level of thermal agitation to the material.

Iron Powder (Fe) and Aluminum Clip (Al) Usage

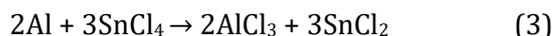
In the chapter "Determination Method Advocated" (JJ Brringer,1925), has also explained that the use of Pure Fe is very effective in removing Cu, Sb, As and others from ore. Basically, there are many alternative ways that can be used in reducing Stanic solution (SnCl₄) so that it becomes a Stannous solution (SnCl₂) which is ready for titration .



What needs to be to known is that the use of pure Fe as a reducing agent must be done in a

strong acid such as HCl (1: 1) and dissolved in a temperature of 250 °C - 350 °C for at least 25 minutes for maximum dissolution. (JJ Brringer,1925) suggests the use of pure Fe from "Iron horseshoe nails" as a reducing source [1], but in an experiment the authors modified the Fe source from Fe Reduced powder (>99,5%, Merck Germany) with a content of 55.85 grams per mole and a maximum powder size of 10 micrometers (µm). The use of clip aluminum (Al) aims at the same thing, with the assumption

that Al will reduce the remaining SnCl₄, which is not completely reduced by Fe to SnCl₂ according to the following reaction:



Modification of the method to determine the level of Sn provides a significant difference when compared to the classical standard method (SNI 13-6348-2000) that is commonly used. For details on these differences can be seen in Table 2.

Table 2. Some Differences between Modified and Classical methods at each stage

Stages	Description	Modified	Classical(SNI 13-6348-2000)
Preparing	milling	same	same
	Measured	same	same
Fusion / Decomposition	Process Media	Crucible ceramic 8 ml disposable	50 ml zirconium used repeatedly
	Heating	Zinc	+ Sodium
	Other Materials		Sulfurcarbonate
	Reductor leaching	Sodiumhydroxide	Sodium hydroxide is required removal of the sample and the washing process need additional HCL 150 + (washing 30 ml to 50 ml), and the risk of spilling, leaching less net
leaching		With crusible 8 ml then do not have to transfer of the sample to the flask HCL = 150 ml	
Finishing	reduction	Fe (iron) + Al (Aluminum)	Only Al (Aluminum)
	Cooling	same	same
	Tittrasi	same	same

RESULTS AND DISCUSSION

Validation of Methods

Data Test Results, Average Value (\bar{x}), Standard Deviation Value (SD) and Standard Deviation Relative Value (RSD)

In this experiment, analysis of 25 reference samples or Certified Reference Materials. From these data the first step will be determined value of Average, Standard Deviation, and Relative Standard Deviation

The average value of the test data were obtained by using the Equation (4)

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (4)$$

\bar{x} is the average value, x_i is the 'i'-data and n is the amount of data. To see the variation in the distribution of the data obtained, it is necessary

to determine the standard deviation value using the following Equation (5).

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (5)$$

SD is the standard deviation. The relative value of standard deviation (RSD) is determined using the following Equation (6) .

$$RSD = \frac{SD}{\bar{x}} \times 100\% \quad (6)$$

From the calculation results obtained for all three parameters values as shown in Table 3 .

Table 3. Value Average, SD and RSD

Parameter	Values
The average value (\bar{x})	62.45%
Standard Deviation (SD)	0.1316
Relative Standard Deviation (RSD)	0.21%

Precision

The precision value of the test data in Table 3 is determined by evaluating the value of repeatability or the relative standard deviation in Table 3 obtained and comparing it with the value of 0.5 CV Horwitz. The value of 0.5CV Horwitz itself is determined by the Equation (7) (Hadi *et. al*, 2018).

$$0.5 CV_{Horwitz} = 0.5x2^{1-0.5\log\log C} \quad (7)$$

The value of c is a constant of the average value of the analyte content / concentration from the test results, in this test the value of c is :

$$c = \frac{62.45}{100} \quad (8)$$

From Equation (8) , the value for 0.5 CV Horwitz is 1.07, so it can be concluded that $RSD < 0.5CV$

Horwitz so that the results of repetition of testing in Table 3 above are still included in the acceptance criteria.

Accuracy

In this test, the method used to show the accuracy of the measurement or test is the parameter of the truth value (Trueness) and the percent of bias. Trueness itself is a method by directly comparing the value of the Certified Reference Material (CRM) test results with the value stated on the CRM certificate. Mathematically the Trueness value is formulated as follows (Hadi, 2017).

$$Truenees(\%) = \frac{\bar{x}}{\mu} x 100\% \quad (9)$$

\bar{x} is the average value listed in table 5 and μ is the grade value stated on the certificate. In this test the CRM used was CRM NCS DC 35002 with a grade value for Sn (Stannum) on the certificate (62.49 ± 0.06)%. So by entering the average value in table 5 into Eq (9), the Truenees value is 99.9%. Percent bias value is obtained using the Eq(10).

$$Bias(\%) = \frac{\bar{x} - \mu}{\mu} x 100\% \quad (10)$$

With the same data using Eq (10), the% bias value is - 0.06%. The Truenees Percent Value itself is still in the range of 99.9% and 0.06% bias with the average test value still included in the interval value stated on the CRM certificate so that it can be concluded that the accuracy value in this test is acceptable.

MDL (Method Detection Limit)

There are two parameters that are determined in finding the MDL value in this test. The first is the detection limit, the detection

limit is determined by the following equation (Riyanto, 2014):

$$Detection\ Limit = 3.143 x SD \quad (11)$$

As for the Quantization Limit, it is determined by the following equation:

$$Limit\ Quantization = 10 x SD \quad (12)$$

So that by entering the SD value contained in (Table 3), the Detection Limit and Quantization Limit values are 0.4 % and 1.32 %, respectively. The LOQ value shows that the modified method can also be used for tin analysis of low concentration.

Ruggedness and Robustness of Method

In the process of determining these parameters, the test is carried out by two different analysts, each test five times at different times and with a titration process using a stirrer and manual. Furthermore, the test results from two different analysts are shown in Table 4. While the acceptance value of this parameter is to compare it with the value (2/3 CV Horwitz) or written in the Eq (13) (Barwick *et. al*, 2014).

$$2/3 CV_{Horwitz} = 2 / 3x2^{1-0.5\log\log C} \quad (13)$$

Where C is the Grand Mean constant from both tests by two different analysts. From the calculations using equation 13 above, the value for (2/3 CV Horwitz) is 1.4. This value indicates that $RSD < 2/3 CV$ Horwitz and it can be concluded that this value is acceptable.

Comparative Test Results with Classical Methods

In this experiment, testing was also carried out using two methods, namely methods that have been modified with classical or standard methods (SNI 13-6348-2000). Tests were carried out in the same laboratory and different analysts with the sample analysis in the form of CRM NCS DC 35002 with a Sn content on the certificate of 62.49%. Each method analyzes the CRM sample in triplo. The results of the analysis can be seen in Table 5. Table 5 shows that the modified method produces biased smaller percent parameters than the classic method did. This proves that the modified method provides better accuracy.

Table 4. Test Results by two analysts A and B

Number Of Test	Concentration A (%)	Concentration B(%)
1	62.23	62.37
2	62.49	62.35
3	62.43	62.52
4	62.68	62.47
5	62.66	62.57
Means	62.50	62.45
SD	0.1836	0.0951
RSD	0.29	0.15

Evaluation

Grand Mean : 62.47

SD :0.1398

RSD :0.22

2/3 CV Horwitz : 1.4

RSD<2/3 CV Horwitz

Table 5. Comparative Test Results between modified and classic method

Modified Method		Classical Method (SNI 13-6348-2000)	
Number of Tests	Concentration (%)	Number of Tests	Concentration (%)
1	62.37	1	62.00
2	62.37	2	61.87
3	62.40	3	62.21
x	62.38	x	62.03
SD	0.0173	SD	0.1716
%Bias	0.0018%	%Bias	0.0074%
MR	99.82%	MR	99.26%

CONCLUSION

Based on the values of the validation parameters obtained in testing this modified method, it shows that all test parameters are included in the required acceptance intervals so that it can be concluded that the method of determining the level of Sn (Stannum) in the modified Tin Concentrate is effective to use. In addition to being viewed from the acceptance parameters of validation, this method is also proven to be good in eliminating negative analysis errors.

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