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UNCERTAINTY OF IODINE VALUE DETERMINATION IN PALM OLEIN

(Ketidakpastian Penentuan Nilai Iodin dalam Minyak Sawit Olein)

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Abstract

The uncertainty of the iodine value determination in refined, bleached, and deodorised palm olein was investigated and calculated. The major sources of measurement uncertainty were identified as the mass of the sample, the molarity of sodium thiosulfate ($Na_2S_2O_3$) solution, the volume of the titrant, the repeatability, and the recovery of the method. The uncertainty sources were quantified according to the law of propagation of errors, standardised, and then combined. The expanded uncertainty calculated was 56.8 ± 1.2 (2.2%). The measurement uncertainty was compared to the precision data of the method, i.e. the repeatability limit. Good agreement was found, which indicated that the major uncertainty sources had been identified. The study also showed that the major sources of uncertainties were contributed by the repeatability component, which will be the main focus in reducing the uncertainty of the iodine value determination.

Keywords: iodine value, palm oil, measurement uncertainty, precision, repeatability limit

Abstrak

Ketidakpastian dalam penentuan nilai iodin di dalam minyak sawit olein yang ditapis, diluntur, dan dinyah bau telah dikaji dan dikira. Sumber utama bagi ketidakpastian penentuan ini adalah berat sampel, kepekatan larutan natrium tiosulfat ($Na_2S_2O_3$), jumlah titran, kebolehulangan dan perolehan semula. Sumber-sumber ketidakpastian telah dikira mengikut hukum penyebaran ralat, dipiawaikan dan kemudian digabungkan. Ketidakpastian terkembang yang dikira adalah 56.8 ± 1.2 (2.2%). Ketidakpastian pengukuran telah dibandingkan dengan data ketepatan kaedah, iaitu had kebolehulangan. Nilai ketidakpastian dan had kebolehulangan bagi kedua-dua data adalah setara dan ini menunjukkan bahawa sumber-sumber utama ketidakpastian telah dikenalpasti. Kajian ini juga menunjukkan bahawa sumber utama ketidakpastian disumbangkan oleh komponen kebolehulangan, yang akan menjadi fokus utama dalam mengurangkan ketidaktentuan untuk penentuan nilai iodin.

Kata kunci: nilai iodin, minyak sawit, ketidakpastian penentuan, ketepatan, had kebolehulangan

Introduction

Iodine value (IV) is one of the most widely used parameters to determine the quality of vegetable oils 1. IV is often used to assess the unsaturation level of oils, which is contributed by fatty acid chains. This unsaturation is represented by double bonds that react with iodine compounds. Consequently, the amount of double bonds present in the oil is proportionate to the iodine number [1]. It can also serve as an indication of the type of oil and its purity with reference to the chemical characteristics of the oil. Saturated vegetable oils, e.g., coconut oil and palm kernel oil, have low IV, whereas unsaturated oils, e.g., olive oil and soybean oil, have higher IV.

In the palm oil industry, IV is used as one of the trading specifications worldwide. Palm Oil Refiners Association of Malaysia (PORAM) established the quality specifications for refined palm oil products, and these formed the normal specifications for refined oil trade based on the Federation of Oils, Seeds, and Feeds Association (FOSFA) free-on-board (FOB) contract for bulk oils. These normal specifications are generally referred to as the PORAM specifications, which are accepted for international trading of refined palm oil products in bulk. The minimum specification of IV for refined, bleached, and deodorised palm olein (RBDPOo) is 56 [2]. The specifications of palm olein are also given in the Malaysian Standard, where the standard palm olein has an IV of 56.0-59.1 [3].

When reporting the result of an analysis, it is important to give some quantitative indications of its uncertainty. The evaluation of measurement uncertainty enables analytical laboratories to measure the quality and to compare analytical results. The measurement uncertainty is defined by ISO as a parameter associated with the result of a measurement that characterises the dispersion of the result that could reasonably be attributed to the measurand [4]. The ISO Guide to the Expression of Uncertainty in Measurement (GUM) recommends uncertainty to be estimated from its components and by applying the law of propagation of errors to combine uncertainties into the total uncertainty. EURACHEM has subsequently interpreted this ISO guide for analytical chemistry [5].

In this work, the uncertainty components and the combined uncertainty of a standard method for the determination of IV in RBDPOo were evaluated. The objectives are to determine the major sources of uncertainty and to subsequently reduce the overall measurement uncertainty of the result.

Materials and Methods

Chemicals and standards

The samples used in this work were RBDPOo (Sime Darby Jomalina, Malaysia). The reagent for diluting the samples was prepared by mixing cyclohexane and acetic acid at 1:1 ratio. Wijs solution was purchased from Merck (USA) and used without further modification. Potassium iodide (KI) solution was prepared by dissolving 100 g of reagent-grade KI in 1000 mL of deionised water to produce a 10% solution. 0.1 M sodium thiosulfate ($Na_2S_2O_3$) solution was prepared from reagent-grade $Na_2S_2O_3 \cdot 5H_2O$. Starch indicator solution was prepared by initially making a paste with 1 g of natural, soluble starch and a small amount of cold distilled water. Boiling water was then added to make up to 100 mL. A reagent-grade potassium dichromate ($K_2Cr_2O_7$) was dried at 110 °C for 2 hours prior to use.

Procedures

The evaluation of the uncertainty of IV determination was done by describing the method, specifying the measurand, identifying uncertainty sources, quantifying the uncertainty components, and calculating combined and expanded uncertainty.

Description of the method

IV was determined according to the standard method AOCS Cd 1d-92 [6]. A molten sample was filtered and weighed into an iodine flask. A mixture of cyclohexane and acetic acid was added to dilute the sample. After the addition of Wijs solution, the iodine flask was stored in the dark for 1 hour. After the required reaction time, 20 mL of 10% KI solution was added, followed by distilled water. The sample was then titrated with 0.1 M $Na_2S_2O_3$ solution until the yellow colour almost disappeared. The

starch indicator solution was added, and the titration was continued until the blue colour disappeared. A blank determination was conducted where no molten sample was added.

An amount 0.1 M $Na_2S_2O_3$ solution was also standardised according to the method AOCS Cd 1d-92. Dried $K_2Cr_2O_7$ was dissolved in distilled water before 5 mL of concentrated hydrochloric acid (HCl) and 20 mL of 10% KI solution were added. The solution was then titrated with the prepared $Na_2S_2O_3$ solution until the yellow colour almost disappeared. The starch indicator solution was added, and the titration was continued until the blue colour just disappeared.

Specification of the measurand

IV was calculated as:

$$\text{Iodine Value} = \frac{(B-S)\times M\times 12.69}{m} \quad (1)$$

where B is the volume of titrant of blank (ml), S is the volume of titrant of sample (ml), M is the molarity of $Na_2S_2O_3$ solution, and m is the mass of sample (g).

The molarity of $Na_2S_2O_3$ solution was calculated as:

$$\text{Molarity of } Na_2S_2O_3 = \frac{W\times 20.394}{V} \quad (2)$$

where W is the mass (g) of $K_2Cr_2O_7$ and V is the volume of titrant (mL).

Identification of uncertainty sources

One of the common tools for the determination of uncertainty sources is the Ishikawa diagram, which is also known as the fishbone diagram or causes and effects diagrams. Therefore, the Ishikawa diagram was created (Figure 1) in order to identify measurement uncertainty components. The figure presents a simplified review of all registered measurement uncertainty causes and shows other potential uncertainty sources that need to be investigated.

The main sources of uncertainty in the measurements were identified as the mass of sample (m), the molarity of $Na_2S_2O_3$ solution (M), the volume of titrant of blank (B), the volume of titrant of sample (S), the repeatability (rep), and the recovery (rec). Uncertainty due to sampling was not considered because the samples in the laboratory were received from the customer who requested the analyses.

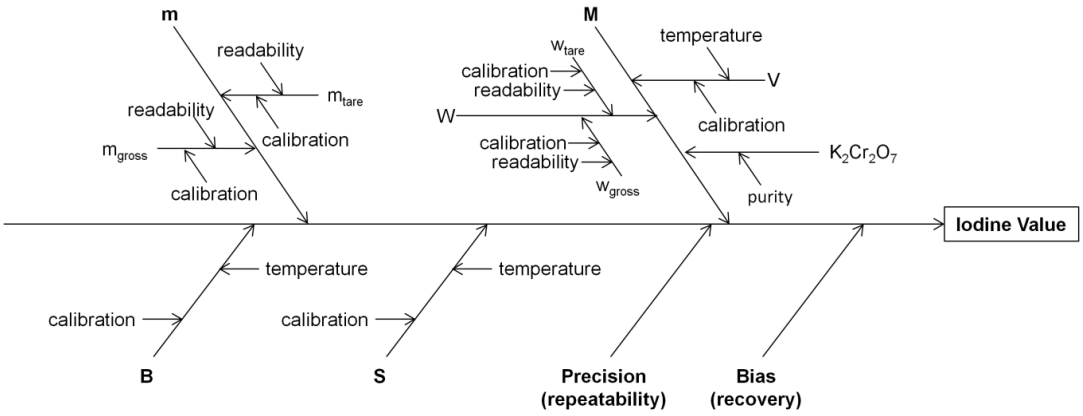

Figure 1. Ishikawa diagram for the determination of iodine value

Quantification of uncertainty components:
Uncertainty associated with weighing operations, u_m
The usual identified uncertainty sources for weighing operations are linearity, readability, sensitivity, and repeatability of a balance [5, 7]. In this work, the linearity and readability (i.e., digital resolution) of the balance used are two potential uncertainty sources. The linearity was obtained from the manufacturer's certificate, where it was reported with a 95% confidence level and converted to a standard deviation by dividing it with a factor of 2. The readability is assumed as a rectangular distribution and its standard uncertainty is obtained by dividing the value given by 2 and √3. The repeatability component is included in the precision estimation whereas the sensibility is neglected because the mass was weighed using the same balance over a very narrow range [5, 8]. The uncertainties should be counted twice because two successive weighing were used, and they are combined as given by Eq. (3).

Uncertainty associated with volumetric operations, u_v
The uncertainty of volumetric operations is associated with the calibration of burette, the use of burette at a temperature different from the one in the calibration, and the repeatability of volumetric deliveries [5, 7]. The limits of accuracy of the burette used (i.e., tolerance) are given by the manufacturer. Since no data on the distribution is reported, a rectangular distribution was assumed as the values are expected to be more likely in the centre than near bounds. The standard uncertainty is obtained by dividing the value given by √3. According to the manufacturer, the burette used has been calibrated at 20 °C, although the temperature in the laboratory varies around 20 ± 4 °C. The uncertainty associated with the temperature can be estimated from the temperature range and the volume expansion coefficient. The volume expansion of water is considerably larger than glass. Therefore, the water volume expansion coefficient is considered as 2.1×10^{-4} °C^{-1}. The repeatability component is included in the precision estimation. In these conditions, the uncertainty associated with the volumetric operations is given by Eq. (4).

Uncertainty associated with reagent purity, u_{pur}
The uncertainty of $K_2Cr_2O_7$ purity was determined from the manufacturer's indications. Since there were no data on distribution, a rectangular distribution was assumed and therefore, u_{pur} is given by Eq. (5).

Uncertainty associated with precision (repeatability)
The method for IV determination is applicable to all normal fats and oils with IV in the range of 18-165 which do not contain conjugated double bonds [6]. The method's precision, in terms of repeatability, may constitute an important source of uncertainty, and hence needs to be studied comprehensively to avoid overestimation or underestimation of the combined uncertainty. The uncertainty associated with the repeatability of IV determination, expressed as a standard deviation, was determined by analysing 23 RBDPOo samples.

Uncertainty associated with bias (recovery)
The method for IV determination is an empirical method where the measurand is defined by the method. The bias of the method is zero by definition when it is used within its defined scope of application [4, 5]. The bias was estimated by the verification of the laboratory implementation of the method according to the parameters influencing the result. The laboratory performance of the method was verified by analysing a certified reference material (CRM) and by performing significance *t*-test. The significance *t*-test indicated that the result of the measurement was not significantly different from the certified value.

$$u_m = \sqrt{2\left({u_{m,linearity}}^2 + {u_{m,readability}}^2\right)} = \sqrt{2\left(\left(\frac{unc}{2}\right)^2 + \left(\frac{R}{2\sqrt{3}}\right)^2\right)} \quad (3)$$

$$u_v = \sqrt{u_{v,calibration}{}^2 + u_{v,temperature}{}^2} = \sqrt{\left(\frac{tolerance}{\sqrt{3}}\right)^2 + \left(\frac{4\times2.1\times10^{-4}\times V}{\sqrt{3}}\right)^2} \quad (4)$$

$$u_{pur} = \frac{100-purity}{2\sqrt{3}} \quad (5)$$

Calculation of combined and expanded uncertainty

The result of a measurement is generally determined from other quantities and the relationship between the result Y and the values of the input parameters can be expressed by Eq. (6).

The uncertainty of the result (u(Y)) depends on the uncertainty of the input parameters and is described by Eq. (7) following the law of propagation of errors.

The sensitivity coefficient describes how the measurement result varies with changes in the value of input estimates. Eq. (7) is valid for measurements where there is no correlation between input parameters.

The relationship between the uncertainty of IV (u(IV)) and the uncertainty of the independent input quantities, which is not correlated, is expressed by Eq. (8).

An expanded uncertainty at 95% confidence level is obtained by multiplying the combined uncertainty with a coverage factor (k) of 1.96. The standard uncertainties, i.e., u(M), u(m), and u(B-S) constituted various uncertainty contributions obtained from uncertainty budgets.

Relative uncertainty variance contributions were used to show the relative impact of different uncertainty components. The relative uncertainty variance contribution (r_i) of an uncertainty component X_i to the combined standard uncertainty, expressed in %, is defined in Eq. (9).

$$Y = f(X_1, X_2, \dots\dots\dots, X_i, \dots\dots\dots, X_N) \quad (6)$$

where X_1,....., X_i,...., X_N represent the model input parameters.

$$u(Y) = \sqrt{\sum_{i=1}^{N}\left(\left(\frac{\partial Y}{\partial X_i}\right)^2 . u(X_i)^2\right)} \quad (7)$$

where $u(X_i)$ are the standard uncertainties of the input parameters and $\delta Y/\delta X_i$ is a sensitivity coefficient.

$$u(IV) = \sqrt{\begin{matrix}\left(\frac{(B-S)\times12.69}{m}\right)^2 . u(M)^2 + \left(-\frac{(B-S)\times M\times12.69}{m^2}\right)^2 . u(m)^2 + \\ \left(\frac{M\times12.69}{m}\right)^2 . u(B-S)^2 + \left(\frac{(B-S)\times M\times12.69}{m}\right)^2 . u(rep)^2 + \\ \left(\frac{(B-S)\times M\times12.69}{m}\right)^2 . u(rec)^2\end{matrix}} \quad (8)$$

$$r_i = \frac{\left(\frac{\partial Y}{\partial X_i}\right)^2 . u(X_i)^2}{u(Y)^2} . 100 \quad (9)$$

where Y is the model equation ((Y=f(X_1, X_2, ..., X_i, ..., X_N)), X_i are the input parameters of the model, and u(Y) is the combined uncertainty calculated according to Eq. (7).

Results and Discussion

The values of the input quantities, i.e., M, m, B-S, rep, and rec, as well as their respective standard uncertainty are listed in Table 1. Standard uncertainties of the model input quantities were also based on uncertainty budgets and calculated according to Eq. (7). The details for M are presented in Table 2.

The result of IV determination was 56.8 g I_2/100 g sample and the evaluated combined uncertainty was 0.6 g I_2/100 g sample, which corresponded to a relative standard uncertainty of 1.1%. An expanded uncertainty at 95% confidence level was obtained by multiplying the combined uncertainty with a coverage factor (k) of 1.96. As a result, the expanded uncertainty of the result of measurement was 56.8 ± 1.2 g I_2/100 g sample (2.2%). The calculated measurement uncertainty was very close to the repeatability limit of the method, i.e., 0.8 g I_2/100 g sample.

The relative variance contributions (r_i) from single input quantities, i.e., u(M), u(m), u(B-S), u(rep), and u(rec) are presented in Figure 2. The largest contribution came from u(rep), which contributed 86.8% to the combined standard uncertainty variance. The volumes of $Na_2S_2O_3$ for the titration of the blank and the sample (B-S) contributed 10.8%. Uncertainty contributions from other input quantities, such as the mass of the sample (m), the molarity of $Na_2S_2O_3$ (M), and recovery are of minor importance.

The development of the measurement uncertainty budget can be a useful tool to reduce uncertainties. In this study, the uncertainty associated with the repeatability component accounted for more than 80% of the uncertainty of IV determination. Several reports have shown that the most effective way to reduce uncertainty contributed by repeatability component is by expanding the number of replicates [10, 11].

The calculation of combined measurement uncertainty reported here considered all uncertainty sources to assess the contribution of each of the uncertainty components and their influence on the final result. Studies on metrological evaluation of IV determination which had been previously reported elsewhere, have not identified the biggest contributor to the measurement uncertainty [12, 13]. Finally, the knowledge of the measurement procedure is as important as the result of the measurement uncertainty calculation.

Table 1. Uncertainty components (u_{xi}) of IV, their standard uncertainty, sensitivity coefficient, and relative variance contribution

Component (X_i)	**Symbol**	**Value (X_i)**	**Standard Uncertainty (u_{xi})**	**Sensitivity Coefficient ($\delta Y/\delta X_i$)**	**Relative Variance Contribution (r_i, %)**
Molarity of $Na_2S_2O_3$ (mol L^{-1})	M	0.1	8.5×10^{-5}	568	0.6
Mass of sample (g)	m	0.2079	7.1×10^{-5}	273	0.1
Volume of titrant (ml)	B-S	9.3	0.0331	6.11	10.8
Precision (repeatability)	rep	1	0.0101	56.80	86.8
Bias (recovery)	rec	0.9995	0.00142	56.83	1.7

IV = 56.8, u(IV) = 0.6

Table 2. Uncertainty components (u_{xi}) of M, their standard uncertainty, sensitivity coefficient, and relative variance contribution

Component (X_i)	**Symbol**	**Value (X_i)**	**Standard Uncertainty (u_{xi})**	**Sensitivity Coefficient ($\delta Y/\delta X_i$)**	**Relative Variance Contribution (r_i, %)**
Purity of $K_2Cr_2O_7$	pur	0.999	2.9×10^{-4}	0.1	11.5
Mass of $K_2Cr_2O_7$ (g)	W	0.1794	8.2×10^{-5}	0.56	28.4
Volume of titrant (ml)	V	36.6	0.024	0.0027	60.1

M = 0.1 mol L^{-1}, u(M) = 0.000085 mol L^{-1}

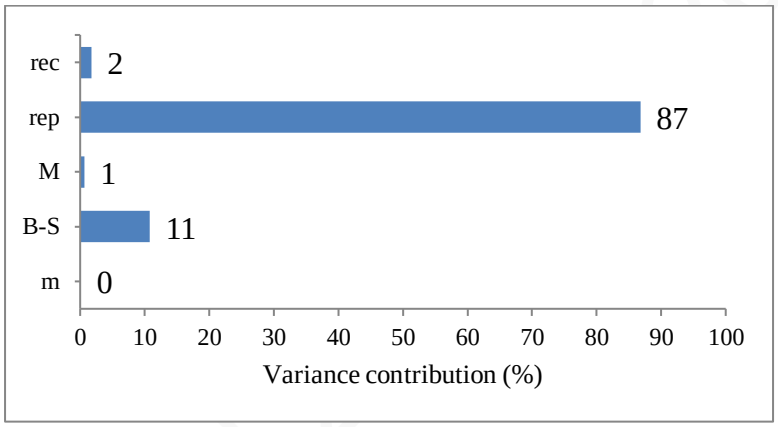

Figure 2. Relative variance contributions from single input quantities to the uncertainty of IV determination

Conclusion

The measurement uncertainty of IV determination of RBDPOo was investigated. The employment of the Ishikawa diagram has allowed the identification of the major uncertainty components and offered a tool for improving the method performance. The uncertainty components were organised in tables, which subsequently facilitated the quantification and estimation processes. Systematic uncertainty budgets have allowed an easy uncertainty evaluation process and enabled a straightforward comparison of the contributions of uncertainty components to the total uncertainty budget. The results revealed that repeatability is the prevailing source of uncertainty. The estimation of measurement uncertainty will be done with a larger number of samples and other palm oil products, e.g. crude palm oil and palm stearin. The IV determination can also be carried out using secondary NIR spectroscopy method and metrological evaluation of the method can be investigated further.

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