Characterization of Fe, Ni, Pb Standard Solution using One-point Calibration Methods

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Abstract. Calibration of measurement systems using well-prepared calibration materials is an important means of making traceability in chemical measurements. Traceability is established through the use of measurement standards (such as certified reference materials) that are appropriate for each parameter. Pure substance certified reference materials such as elemental standard solutions are the most commonly used for calibration, called external calibrations using one, two or multiple standards. In this study, one-point calibration method has been applied for characterizing of Fe, Ni and Pb standard solutions. The results show that the concentration of the Fe, Ni and Pb standard solutions with their relative uncertainties were found to be 997.81 ± 6.34 mg/kg, 997.61 ± 8.10 mg/kg, 1004.29 ± 8.62 mg/kg, respectively.

1. Introduction
Characterization is one of the most important steps for assigning reference value of any reference materials (RM). The reference value with measurement uncertainty is given with traceability statement to a certified reference materials, reference measurement procedures or comparison of measurement standards. The measurement procedure is acceptable when it provides an appropriate measurement result for the intended use in determining the measured values obtained from other measurement procedures for the sum of the same type, in calibration, or in the characterization of the reference material [1].

Calibration of measuring instruments is an essential part of the laboratory measurement activity in the field of analytical chemistry [2]. Based on International vocabulary of metrology (VIM) calibration is defined as the activity undertaken under certain conditions, by the first step, to determine information about the relation between the value and uncertainty of a standard with the measurement of the standard, and in the second step, using this information to determine value and uncertainty of measurement results from samples [1].

Calibrants are measurement standard specifically used in calibrating, also called as “calibrators” in analytical sciences, reference materials that are classified in two types: substance RM which is used for the proposed calibration and matrix reference materials. Substance RM is prepared from single analyte including pure substances or standard solutions [3,4].

Primary solutions prepared from the materials or solutions are widely used for calibration in many fields of application [5]. The purpose of the calibration in chemical measurement is to establish a
quantitative relative between several known concentration and their corresponding signals, thus yielding a response curve [6].

Methodological approaches to calibration considering the number of standards employed to perform the calibration by using: 1). A single concentration of chemical standard, the one-point calibration, 2). Two concentrations of chemical standard, the double-point calibration, and 3). Three or more concentrations of chemical standard, the multiple-point calibration [6].

The one-point calibration is used when the instrumental response is strictly proportional to the amount of analyte [7]. The response factor (F) which is determined using equation (1)

\[
F = \frac{y_{cal}}{x_{cal}}
\]

where \(y_{cal}\) is refer to the mean value of response and \(x_{cal}\) is the reference value of analyte amount. The response factor is then used to convert instrumental response data \(y_{spl}\) obtained on other samples into analyte amounts \(x_{spl}\) according to equation (2)

\[
x_{spl} = \frac{y_{spl}}{F}
\]

Equations (1) and (2) illustrate the two steps in calibration, establishing a relationship between reference value \(x_{cal}\) and response \(y\), and then using this to derive a calculation to predict values \(x_{spl}\) [7].

One point calibration is for single concentration of analyte, which is only use one standard concentration as a reference for calculating the concentration of analyte in the sample. One-point calibration use to be applied in routine analysis when the expected range of the analytes concentrations is small and in a direct calibration. For example, in clinical laboratories where many automated analyzers use only a single standard and in the conductimetric calibration with KCl standard solution [4,6]. The two standard calibrations, also called double point calibrations, define an interval of the analyte concentrations in the sample. Double point calibrations are routinely used in laboratories for calibrating pH-meters and for analyzing pesticide residue. Meanwhile, multiple point calibration use at least three concentration level of standards, and the expected analyte concentration should be in the range of the set concentration standards. The multiple point calibration used to be applied in routine laboratories with variety of samples [4,6].

The result of a calibration, whether it is calculated using a factor or a function summarizing the calibration data, has an associated uncertainty. In the case of one-point calibration, by combining equation (1) and (2), the equation could be expressed in equation (3) and the uncertainties directly associated with calibration may be expressed as equation (4) [7]. This method is evaluated in accordance with ISO Guide to the expression of uncertainty in measurement (GUM) guidelines [1] and EURACHEM [8].

\[
x_{spl} = \frac{y_{spl}}{y_{cal}} \cdot x_{cal}
\]

\[
\frac{u_{cal}(x_{spl})}{x_{spl}} = \sqrt{\left(\frac{s(y_{spl})}{y_{spl}}\right)^2 + \left(\frac{s(\bar{y}_{cal})}{\bar{y}_{cal}}\right)^2 + \left(\frac{c(x_{cal})}{x_{cal}}\right)^2}
\]

The one point calibration method has been known and applied successfully using various instrument techniques. Peel et.al showed the accurate mass bias correction and precise Zn and Cu isotope ratio measurements with modified sample-standard bracketing technique [9,10]. Yuan et al. combined standard-sample bracketing calibration method with Mg as an internal standard for silicon isotopic compositions using multi-collector inductively coupled plasma mass spectrometry [11]. Sheila Merson and Peter Evan use an ICP-OES for the high accuracy analysis of minor elements in steel [12].

Recently, the pilot study of Asia Pacific Metrology Program (APMP) Calibration Solution (APMP.QM-P30) was a jointly organized by National Measurement Institute of India (NPLI) and
Korean Research Institute of Standards and Science (KRISS). The reference values in this study were provided by KRISS, National Institute of Metrology, China (NIM), and National Metrology Institute of Japan (NMIJ). The aim of this study was to prove capabilities of the participants have to measure high concentration sample solution (1000 mg/kg) with small uncertainty (< 1%) [13]. This study reports the participation of the Research Centre for Metrology-LIPI (RCM-LIPI) on the APMP Pilot Study (APMP.QM-P30) for the measurement of Fe, Ni and Pb standard solution by ICP-AES. This ICP-AES technique is commonly used for the analyte measurement in the production of reference materials and standards [12].

2. Material and Methods

2.1 Instrumentation
All measurements were conducted using the ICP-AES Vista AX (Varian, Melbourne, Australia). The operating conditions of ICP-AES are listed in table 1. Accurate dilution of the standard solutions was carried out by weighing using analytical balance AND GR200 (Tokyo, Japan).

| Conditions               | ICP-AES Varian |
|-------------------------|----------------|
| Plasma gas (L min⁻¹)    | 15             |
| Auxiliary gas (L min⁻¹) | 1.5            |
| Nebulizer gas (L min⁻¹) | 200            |
| Power (kW)              | 1.1            |
| Viewing                 | Axial          |
| Sample uptake (ml min⁻¹)| 10             |

2.2 Reagents and Solutions
Nitric acid (60%) for poisonous metal was purchased from Kanto Chemicals (Tokyo, Japan). Ultra-pure water produced from a milli-Q Plus 185 with 18.2 MΩ/cm resistivity were used in all experiment runs (Mosheim, France). All standard and samples were put in the clean Nalgene HDPE bottles 125 mL and HDPE conical centrifuge tubes 50 mL from Thermoscientific (New York, USA). The calibration graph for Fe, Ni, and Pb were prepared using standard solution reference materials SRM 3126aFe (NIST, USA), SRM 3136Ni (NIST, USA), and Pb 0001-BAM-Y004 (BAM/PTB Germany), respectively. In this study, the sample solution (APMP.QM-P30 elemental standard solution) was prepared and provided by NPLI for APMP pilot study. The sample solution was used as received without any further treatment.

2.3 Procedure for measuring the Fe, Ni and Pb
Sample of elemental standard solutions was prepared gravimetrically using available respective pure metals at nominal concentration (mass fraction) 1000 mg/kg in 5% nitric acid. Therefore 5% nitric acid was used to prepare all standard solution in order to have similar matrix with the sample. The sample was diluted to 20 times for Fe, Ni and Pb determination and then measured by ICP AES through one point calibration. Each element measured with multiple wavelength and the standard solutions prepared by three different analyst. The sample was measured by bracketing technique using pre-sample and post-sample calibration standard as follows: Standard 1 – Sample – Standard 1 – Sample –Standard 1 – and so on. The concentration of the target analytes in the sample was calculated from the mean.

3. Results and Discussion
Calibration of a measurement system by using properly prepared calibration materials is the essential means of establishing traceability for chemical measurements [14]. The one-point calibration could be performed from only one calibrant when two conditions are fulfilled: the calibration function must be linear in the interval of analyte amount ranged from the standard value to zero, and the blank signal
must be null in the internal previously referred to. However, the linearity requirement can be avoided when the analyte amount in the selected calibration standard is very near to the one in the sample which is possible when the features of the sample are previously known [3].

The suitability of the single point calibration method increases when the concentration of the standard solution is similar to the expected concentration in the sample solution [6]. This approach is applicable only if the measurement scatter is narrow enough in relation to the precision required for the assay. In this study, both standard and sample have similar concentration. Sample was run in the couple of times in order to get higher precision of the result. As can be seen in table 2, the measurement results of Fe, Ni, and Pb were 997.82, 997.61 and 1004.28, respectively, with their uncertainties were less than 1%. This result is in a good agreement with the reference values of the sample. The reference values is an average value from KRISS, NMIJ, and NIM China.

The possible drift in the calibration factors should be investigated as a measurement bias. The drift may occur when one point calibration is used inappropriately [6]. Instrumental drift continuous or incremental change over time in indication, due to changes in metrological properties of a measuring instrument which is related neither to a change in a quantity being measured nor to change of any recognized influence quantity [1]. The one-point standard calibration by means of bracketing mode was utilized to overcome the instrument drift and increase the precision of measurement [10].

**Evaluation of the measurement uncertainty**

When the one-point calibration method was applied in this study, the equation (3) was then simplify to equation (5) for calculating $x_{spl}$,

$$
x_{spl} = \frac{Y_{spl}}{Y_{std(before&after)}}x_{cal}xDF
$$

Where $x_{spl}$, is refer to concentration of the analytes (Fe, Ni, and Pb) in the APMP sample, $Y_{spl}$ is the intensity of analyte readed by ICP-AES, $Y_{std(before&after)}$ is the intensity of the one-point standard before and after the sample, $X_{cal}$ is the concentration of the analyte which were prepared in the standard and $DF$ is the dilution factor.

**Figure 1.** Cause-and-effect diagram identifying sources of uncertainty elemental standard solution
Figure 1 presents the cause and effect diagram representing the identified sources of uncertainty for the determination Fe, Ni and Pb sample standard solutions. Based on the diagram, it can be clearly seen that main components contributing to the uncertainty are of reproducibility, standard stock and dilution factor.

In this method, the sample is diluted with 5% nitric acid before measured using ICP-AES based on weight per weight calculation. The dilution factor (DF) is given by equation (6) [14].

\[
DF = \frac{m_2}{m_1}
\]

(6)

Where \(m_2\) is mass of sample solution, and \(m_1\) is mass of target analyte. The weight was determined using the same calibrated analytical balance which has standard uncertainty 0.0011 g on 95% confidence level. Therefore, total standard uncertainty \(\mu(DF)\) from these sources was calculated by taking into account all those weight uncertainties as given in equation (7).

\[
\frac{\mu(DF)}{DF} = \sqrt{\left(\frac{u(m_1)}{m_1}\right)^2 + \left(\frac{u(m_2)}{m_2}\right)^2}
\]

(7)

The uncertainty sources from type B (stock) and type A were taking into consideration for calculation the budget uncertainty from standard sources. All values and associated uncertainties are showed on table 2. Based on the table, the main contributed uncertainty is coming from reproducibility sources as the random error. However, the expanded uncertainty for all measurands give less than 1% of the value, and it met the relative target uncertainty of this sample (<1%) which was appointed by the APMP sample provider. The total uncertainty is given in equation (8).

\[
\frac{u(x_{spl})}{x_{spl}} = \sqrt{\left(\frac{s(y_{spl})}{y_{spl}}\right)^2 + \left(\frac{s(\bar{Y}_{cal})}{\bar{Y}_{cal}}\right)^2 + \left(\frac{u(x_{cal})}{x_{cal}}\right)^2 + \left(\frac{u(DF)}{DF}\right)^2 + \left(\frac{Rep}{x_{spl}}\right)^2}
\]

(8)

| Uncertainty components          | Value (x_i)   | Standard Uncertainty (u(x_i)) | Relative Standard Uncertainty (u(x_i)/x_i) |
|---------------------------------|---------------|------------------------------|-------------------------------------------|
|                                 | Fe            | Ni                           | Pb                                         | Fe            | Ni                           | Pb                                         |
| Reproducibility                 | 997.81        | 997.61                       | 1004.29                                   | 2.68          | 3.59                        | 4.26                                      |
| Calibration std Type B          | 10013         | 10003                        | 1000                                      | 1.20E         | 1.32E                       | 4.40E                                    |
|                                 | +01           | +01                          | -01                                       | 1.19E         | 1.31E                       | 4.45E                                    |
| Calibration std Type A          | 49.98         | 50.35                        | 50.01                                     | 5.99E         | 6.64E                       | 2.22E                                    |
|                                 | -02           | -02                          | -02                                       | 1.19E         | 1.31E                       | 4.45E                                    |
| Dilution factor                 | 19.99         | 10.01                        | 20.01                                     | 1.44E         | 5.16E                       | 5.43E                                    |
| C                               | 997.81        | 997.61                       | 1004.29                                   | -05           | -05                         | -05                                      |
| u_c                             | 3.17          | 4.05                         | 4.31                                      | 07            | -06                         | -06                                      |
| U                               | 6.34          | 8.10                         | 8.62                                      | (0.63%)       | (0.81%)                     | (0.86%)                                   |
| Assigned reference value *      | 1000.02       | 1000.44                      | 1002.45                                   | 1000.44       | 1002.45                     | 1002.45                                   |

*The reference values from KRISS, NMIJ, and NIM China.
4. Conclusion

A calibration by using one-point calibration was used for the characterization of the standard solution. This calibration method is usually applied in direct calibration, when the concentration of the standard solution is very close to expected concentration in the sample solution. It can be concluded that we enable to measure elemental standard solution and reduce relative target uncertainty < 1% in APMP Pilot Study (APMP QM-P30) with the concentration of 997.81 mg/kg for Fe, 997.61 mg/kg for Ni, and 1004.29 mg/kg for Pb and the percentage expanded uncertainty of 0.63%, 0.81%, 0.86%, respectively.

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