Development of a rapid-test method for the determination of calcium, zinc, phosphorus, and sulfur in automotive engine oil by WD-XRF (wavelength dispersive x-ray fluorescent)

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Abstract. This study describes a rapid method for the determination of calcium, zinc, phosphorus, and sulfur in lubricating oil products using WD-XRF (Wavelength Dispersive X-ray Fluorescent). Currently, there are several normative references appointed by the mandatory SNI (Indonesian standard) used for elemental analysis in automotive engine oils, i.e., ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy), AAS (Atomic Absorption Spectrophotometry) for calcium, zinc, or magnesium; ED-XRF (Energy Dispersive X-ray Fluorescent) for sulfur, lamp method for sulfur, and quinoline phosphomolybdate method for phosphorus. The wet chemical analysis principle used in those reference methods (AAS, ICP-AES, and conventional method) needs a sample preparation step before the main instrument can use to measure an oil sample. It is a time-consuming process and commonly consists of a few steps such as dilution, weighing, heating, and destruction. The statistical characteristics (limit of detection, the limit of quantification, precision, accuracy, and linearity) obtained in this experiment were relatively acceptable. Elemental analysis by WD-XRF needs no sample preparation step before the main instrument can use to measure an oil sample. It is a time-consuming process and commonly consists of a few steps such as dilution, weighing, heating, and destruction. The statistical characteristics (limit of detection, the limit of quantification, precision, accuracy, and linearity) obtained in this experiment were relatively acceptable. Elemental analysis by WD-XRF needs no sample preparation process, fast, less chemical reagents, multi-elements, simultaneously, and simple. The WD-XRF method potentially could be used as an alternative method for the determination of certain elements (Ca, Zn, P, S) or more as specified in the mandatory SNI for automotive engine oil products.

1. Introduction
Lubrication is one of the critical factors in maintaining engine performance in optimum conditions. The lubricating oil can protect an engine from degradation factors such as wear, heat, corrosion, oxidation, and various contaminant [1]. The quality of oil used in engine parts will affect fuel consumption and exhaust gas. Optimum lubrication can reduce gas emission produced by a combustion engine [2]. Good lubricating oil could preserve engine performance, cost efficiency, less air pollution, and increase safety.

The number of motor vehicles that continues to grow every year will boost the need for lubricants in Indonesia. According to BPS (Statistics Indonesia) data, in 2018 the total number of four types of motorized vehicles (passenger cars, bus cars, freight cars, and motorbikes) reached 146,858,759 vehicles [3]. The need for lubricants for such large numbers of motor vehicles needs to be balanced by reliable lubricant quality.

On September 5, 2018, the Indonesian Ministry of Industry published "Permenperin No. 25 (2018), tentang Pemberlakuan Standar Nasional Indonesia Secara Wajib" which set the mandatory SNI
(Standar Nasional Indonesia) regulation for seven types of automotive engine oil products. Products included in this regulation are: (1) four-stroke gasoline engine oil (SNI 7069.1:2012), (2) four-stroke gasoline engine oil for motorcycle (SNI 7069.2:2012), (3) two-stroke gasoline engine oil with air cooler (SNI 7069.3:2016), (4) two-stroke gasoline engine oil with water cooler (SNI 7069.4:2017), (5) Diesel engine oil high rotation (SNI 7069.5:2012), (6) manual transmission gear oil (SNI 7069.6:2017), and (7) automatic transmission oil (SNI 7069.7:2017). This regulation has been applied effectively since September 10, 2019[3].

The specific element’s content is included in the mandatory SNI specifications. The elements that should be determined in lubricating oil products are calcium, magnesium, zinc, phosphorus, and sulfur. According to the SNI, each element could be analyzed by a few different methods. Table 1 shows the reference methods used in the SNI. Metals content in lubricating oil provided valuable information about its composition, sedimentation of metal parts, or degradation of additive in an engine [4]. Elements contained in automotive lubricating oils were found as impurities or additives. Calcium and zinc in automotive lubricating oil were used as a detergent additive ingredient and anti-corrosion agent [5]. Phosphorus in engine oil was seen as anti-wear/antioxidant additive that, during operation, could be volatilized [6]. Sulfur in engine oil was found as mineral base oil impurities [7]. Heavy metals (Al, B, Cr, Cu, Fe, Pb, Mn, Mo, Ni, Na, Si, Ag, Sn, Ti, V, Cd, and As) in used oil can provide valuable information about wear metals and contaminants [8].

| SNI Specification | Calcium | Zinc | Phosphorus | Sulfur | Magnesium |
|-------------------|---------|------|------------|--------|-----------|
| 7069.1:2012       | D4628/ D5185 | NS* | D4047/ D4951 | D2622/ D4951 | D4628/ D5185 |
| 7069.2:2012       | D4628/ D5185 | D4628/ D5185 | D4047/ D4951 | NS | D4628/ D5185 |
| 7069.3:2016       | D4628/ D5185 | NS | NS | NS | NS |
| 7069.4:2017       | D4628/ D5185 | NS | NS | NS | NS |
| 7069.5:2012       | D4628/ D5185 | D4628/ D5185 | D4047/ D4951 | D2622/ D4951 | D4628/ D5185 |
| 7069.6:2017       | NS | NS | D4047 | D1266 | NS |
| 7069.7:2017       | D4628/ D5185 | D4628/ D5185 | D4047 | D4294/ D6481 | NS |

*NS: Not Specified

The Determination methods of elements content in lubricating oil according to ASTM standards are as follows: (a) Calcium, magnesium, and zinc; tested by AAS (Atomic Absorption Spectrophotometry) [9] or ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy) [10]; (b) Phosphorus tested by quinoline phosphomolybdate method (titration) [11] or ICP-AES [12]; and (c) Sulfur tested by lamp method [13], WD-XRF [14], ICP-AES [12] or ED-XRF [15,16]. The wet chemical analysis technique was used in AAS, ICP-AES, and titration.

Elemental analysis in lubricating oil product using AAS method has a good detection limit [17]. Still, it needs a time-consuming sample preparation process, and cannot be determined multi-elements simultaneously. For ICP-AES, although it has a very low detection limit and could measure multi-elements at once [8], it needs some expensive consumable supporting materials and precise sample preparation process. Titration method for phosphorus determination by quinoline phosphomolybdate is a low-cost method (no need an expensive instrument like AAS, ICP-AES, nor XRF), but it needs a complicated preparation process and more chemicals.
Among the other available analytical techniques, XRF spectrometry potentially can be used as a single method for determining all of the specific elements required by the mandatory SNI specification simultaneously. WD-XRF (Wavelength Diffraction X-Ray Fluorescence) method has developed for the analysis of Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Si, Ti, V, and Zn in various petroleum liquid products with no significant loss of accuracy[18]. The WD-XRF method offers advantages by its minimum preparation, fast, and has an excellent detection limit compared to other elemental analysis techniques.

This study focuses on determining the concentration of selected elements (Ca, Zn, P, and S) in automotive engine oils by using the WD-XRF method for described a simple and fast testing method. Statistical parameters for method validation is also presented [19].

2. Materials and methods

2.1. Materials
ASI (Analytical Services Incorporation) LOE17 was used as Oil Reference Material. Commercial, automotive engine oil that available in markets in Bandung region was used as a lubricating oil sample. Plastic X-ray cell of 25 mm diameter and a plastic film chemically resistance (Mylar®, with 6 μm thickness) was used as a base holder material.

2.2. Instrument
ASI (Analytical Services Incorporation) LOE17 was used as Oil Reference Material. Commercial, automotive engine oil that available in markets in Bandung region was used as a lubricating oil sample. Plastic X-ray cell of 25 mm diameter and a plastic film chemically resistance (Mylar®, with 6 μm thickness) was used as a base holder material.

2.3. Procedures
About 50 mL standard or sample was added to a cell cup then placed in an autosampler holder. The measurement of metals content was performed by WD-XRF Analyzer and controlled by PC. The calibration standards were prepared from CRMs (Certified Reference Materials) diluted by white oil; at least five standards solution were measured to obtain the calibrations curves. The measurement of samples was carried out after the calibration curves were made. Every sample was measured at least three times (triple) to have a representative result. The Limit of Detection (LD) and the Limit of Quantification (LQ) value was determined by measuring a new solution (white oil) or spiked sample for five times. Measured CRM determined the Accuracy and Precision for five times, then compared the value obtained from the measurement with the actual number stated in the certificate. These experiments were evaluated using CRM as a control to ensure the accuracy of the analysis.

3. Result and discussion

3.1. Time of analysis
A simple procedure was applied in this experiment. Lubricating oil sample from the original sealed bottle poured into a cell cup up to volume marker (about 50 ml), then it placed in autosampler holder. The measurement proceeds directly after the cell cup placed in the autosampler holder. The whole process for conducting elemental analysis for a single sample took about 3-5 minutes or less than 5 minutes.

The common elemental analysis method consisted of three necessary steps: sample preparation, measurement, and calculation. The modern analytical instrument commonly had equipped by software that could be used for calculating the instrument data to generate the measurement result, so the count took place during the measurement process. The main issues in the analysis duration were the sample preparation process. The wet chemical sample preparation commonly needed a few procedures, such as weighting, dilutions, and digestion. This process could become an uncertainty contributor and
affected the accuracy of the method. The time needed during a sample preparation process (i.e. weighing, dissolved, making standard solution, and dilution) was varied, depended on the sample characteristics (i.e. solubility, and suspended solid) and instruments (i.e gas type, light source, and compatibility) used. A fast analytical method or rapid-test would have a lot of advantages if applied in-field inspection and quality control processes in the factory. Less chemical means more contribution to green industrial production. Time efficiency would be to reduce the cost of analysis and human resources.

3.2. Limit of detection and limit of quantification

Limit of Detection (LD) or Limit of Quantification (LQ) was commonly defined as the lowest concentration of an analyte that can be detected. Several approaches can be used to estimate LD and LQ, i.e., visual assessment, signal to noise ratio, calculated from the standard deviation of the blank, calculated from the calibration line at low concentration [20]. LD was meant to know the limit test for impurities, and the LQ was to determine the quantitative analysis for the impurities quantification of the main component [21].

The LD and LQ were calculated from the measurement of a spiked sample. The sample was measured seven times under reproducibility conditions. It was calculated by concentration corresponding to the blank or spiked sample plus three standard deviations, as shown in equation 1, and LQ is corresponding to ten standard deviations, as shown in equation 2 [20].

\[
LD = x + 3\sigma \\
LQ = x + 10\sigma
\]

where \(x\) is the mean concentration of the blank or spiked sample, and \(\sigma\) is the value of the standard deviation of the measurements. Although by this method it was difficult to prove that a low concentration of analyte signal was different from the blank signal, it had the benefit as the simplest and fast method that could be used in LD and LQ determination. Table 2 shows that LD (%mass) for Ca = 0.00955, P = 0.00800, S = 0.06907, and Zn = 0.03075; and LQ (%mass) for Ca = 0.01693, P = 0.01277, S = 0.07508, and Zn = 0.03442.

| Element (%mass) | Ca   | P    | Zn   | S    |
|-----------------|------|------|------|------|
| Replicates      |      |      |      |      |
| 1               | 0.00589 | 0.00549 | 0.06590 | 0.02900 |
| 2               | 0.00863 | 0.00588 | 0.06710 | 0.02890 |
| 3               | 0.00548 | 0.00582 | 0.06810 | 0.02940 |
| 4               | 0.00621 | 0.00522 | 0.06660 | 0.02940 |
| 5               | 0.00633 | 0.00591 | 0.06610 | 0.03000 |
| 6               | 0.00567 | 0.00737 | 0.06610 | 0.02830 |
| 7               | 0.00651 | 0.00599 | 0.06560 | 0.02920 |
| Sum (\(\Sigma\)) | 0.04472 | 0.04168 | 0.46550 | 0.20420 |
| Mean (\(x\))    | 0.00639 | 0.00595 | 0.06650 | 0.02917 |
| Standard Deviation (\(\sigma\)) | 0.00105 | 0.00068 | 0.00086 | 0.00053 |
| Limit of Detection (LD) | 0.00955 | 0.00800 | 0.06907 | 0.03075 |
| Limit of Quantification (LQ) | 0.01693 | 0.01277 | 0.07508 | 0.03442 |
3.3. Precision and accuracy

The precision of the method was calculated by analyzing a series of samples from a homogenous solution. The Collaborative International Pesticides Analytical Council Limited (CIPAC) guidelines stated that the repeatability precision would be acceptable if several replicated samples were not less than five replicates and the value of %RSD calculated from measurement less than CV-Horwitz multiple by 0.67[22]. Data from Table 2 shows that the %RSD of analysis for Ca, P, S, and Zn were below the 0.67 x CV-Horwitz value. %RSD was calculated by equation 3, and CV-Horwitz obtained using equation 4.

\[
% RSD = \frac{\sigma}{x} \times 100\%
\]  

(3)

\[
CV-Horwitz = 2^{(1-0.5 \log C)}
\]  

(4)

Where, \(x\) is measurement results, \(\sigma\) is standard deviation of measurement, and \(C\) is measurement results in percent (%).

The measurement result generated the accuracy of the testing method to the actual value stated in CRMs. The accuracy was evaluated by using z-scores (\(z\)), a statistical parameter that indicates how many standard deviations of the measurement results compared with the certified/true value of an element in CRMs, \(z\)-scores was calculated by the equation 5.

\[
z = \frac{x - X}{\sigma}
\]  

(5)

where, \(X\) is the certified value of CRMs (%).

The interpretation of the \(z\)-score is satisfactory if the score not more than 2 (|score| ≤ 2), unsatisfactory if more than 3 (|score| ≥ 3), and questionable if the score between 2 and 3 (2 < |score| < 3)[23]. According to Table 3, the accuracy of the measurement of sulfur, phosphorus, and zinc was satisfied, but for calcium, it needed to be improved.

| Table 3. CRM measurement for precision and accuracy. |
|-----------------------------------------------|
| Replicates | Ca  | P   | S   | Zn  |
|------------|-----|-----|-----|-----|
| 1          | 0.0529 | 0.0253 | 0.1041 | 0.0216 |
| 2          | 0.0491 | 0.0228 | 0.0968 | 0.0199 |
| 3          | 0.0472 | 0.0212 | 0.0958 | 0.0200 |
| 4          | 0.0463 | 0.0212 | 0.0949 | 0.0196 |
| 5          | 0.0456 | 0.0215 | 0.0945 | 0.0195 |
| 6          | 0.0448 | 0.0208 | 0.0946 | 0.0194 |
| 7          | 0.0460 | 0.0204 | 0.0942 | 0.0193 |
| 8          | 0.0457 | 0.0210 | 0.0931 | 0.0193 |
| 9          | 0.0455 | 0.0206 | 0.0931 | 0.0195 |
| 10         | 0.0448 | 0.0202 | 0.0930 | 0.0192 |
| Sum (\(\Sigma\)) | 0.4679 | 0.2150 | 0.9541 | 0.1973 |
| Average (\(x\)) | 0.0468 | 0.0215 | 0.0954 | 0.0197 |
| Standard Deviation (\(\sigma\)) | 0.0025 | 0.0015 | 0.0033 | 0.0007 |
| %RSD | 0.0533 | 0.0706 | 0.0345 | 0.0358 |
| CV-Horwitz = | 3.1710 | 3.5647 | 2.8485 | 3.6111 |
| 0.67 x CV Horwitz = | 2.1245 | 2.3883 | 1.9085 | 2.4194 |
| Reference value (\(X\)) = | 0.0400 | 0.0200 | 0.0900 | 0.0200 |
| z-score = | 2.7248 | 0.9876 | 1.6455 | 0.3826 |
3.4. Calibration curve and linearity

The linearity of response to the analyte concentration should be calculated at least three measurement data. The curve showed no significant deviation from linearity if the correlation coefficient (R²) value was above 0.99 [22]. Interferences and sample matrix need to consider in constructing a working range because obstructions can cause non-linear responses, and sample matrix could change the ability of the method to extract/recover the analyte from the sample. The working range and linearity for this method were assessed by visual inspection of plotted data in the calibration curve supported by statistical linear regression. The calibration curve needed to be established individually for each element and matrix to get a quantitative analysis. Working range proposed for a sulfur determination as shown in figure 1 was between 0.002 to 5 mg/kg with linearity coefficient (R²) value 0.99713, for calcium shown in figure 2 was between 0.0025 to 0.5 mg/kg with linearity coefficient (R²) value 0.99964, for zinc shown in figure 3 was between 0.05 to 0.25 mg/kg with linearity coefficient (R²) value 0.99643, and for phosphorus shown in figure 4 was between 0.002 to 5 mg/kg with linearity coefficient (R²) value 0.99713.

![Figure 1. Calibration curve of sulphur](image1)

![Figure 2. Calibration curve of calcium](image2)

![Figure 3. Calibration curve of zinc](image3)

![Figure 4. Calibration curve of phosphorus](image4)
3.5. Uncertainty of measurement
Sources of uncertainty in XRF spectrometry according to IAEA (International Atomic Energy Agency) consists of six components, i.e., calibration of the spectrometer, instability of spectrometer (detector and electronics), sample preparation (heterogeneity of the material and non-uniformity of sample thickness), spectral data processing with the fitting program, quantification (determination of the absorption correction factor), and uncertainty in the determination of total mass per unit area[24]. The uncertainty contributors in XRF measurement were influenced by the calibration curve, variation of replicates, sample preparation, and influence from operators. Uncertainty contributors from calibration measurements and laboratory analysts were negligible [25].

The estimation of uncertainty is simple in principle. The following approached could use to the quantification of uncertainty associated with a measurement result in different circumstances, i.e., using data from in-house and collaborative method validation studies, Quality Control, Proficiency Testing, relevant prior studies, and the use of formal uncertainty propagation principles [26]. Uncertainty estimation for elemental analysis of lubricating oil by WD-XRF base on the testing process indicated that the best available contributor was from the individual repeatability of the measurement.

3.6. Qualitative and quantitative measurement
WD-XRF is a powerful tool in elemental analysis problems. The method is proposed for qualitative and quantitative analysis of solid material (thin or bulk, alloys or rocks, etc.), with advantages in sample preparation (without treatment, fusion, etc.) and measurement (single or multi-element) [27]. Qualitative and quantitative analysis can be used for the determination of major, minor, and trace elements in various kinds of samples. The qualitative analysis (scanning mode) can be done satisfactorily for automotive engine oil samples, for quantitative analysis depends on the availability of oil standards (CRMs, SRM). Table 4 shows the analysis results for various types of automotive engine oils. The twelve samples sequentially analyzed by WD-XRF and finished in 50 minutes.

Table 4. Analysis of various engine oil samples.

| Nr. | Sample ID | Ca    | P     | S     | Zn    |
|-----|-----------|-------|-------|-------|-------|
| 1   | N2        | 0.2917| 0.0954| 0.2228| 0.1109|
| 2   | LOE17.15  | 0.1037| 0.1018| 0.1980| 0.1904|
| 3   | Oil F1    | 0.2346| 0.0901| 0.3596| 0.1019|
| 4   | Oil F2    | 0.1875| 0.0717| 0.2688| 0.0809|
| 5   | Oil F3    | 0.2532| 0.0989| 0.2825| 0.1126|
| 6   | Oil F4    | 0.2307| 0.0708| 0.2106| 0.0778|
| 7   | Oil F5    | 0.2810| 0.0856| 0.2604| 0.0956|
| 8   | Oil F6    | 0.2807| 0.0848| 0.2552| 0.0944|
| 9   | Oil F7    | 0.2559| 0.0789| 0.2303| 0.0869|
| 10  | Oil F8    | 0.3732| 0.0973| 0.3009| 0.1108|
| 11  | Oil F9    | 0.4225| 0.0751| 0.2258| 0.0854|
| 12  | Oil F10   | 0.3635| 0.0762| 0.2172| 0.0852|

4. Conclusion
WD-XRF method allows the simultaneous determination of certain elements (calcium, zinc, phosphorus, and sulfur) in lubricating oils quantitatively. Complicated sample preparation was not needed, and it was simple in terms of its analysis procedures (no need to burn the sample, heated,
weighted, destruction, etc.), along with less chemical reagents used. WD-XRF offered a fast (rapid-test), low-cost (all elements by single method), and a more environmentally friendly process in elemental analysis of automotive engine oils. The performance characteristics (detection limit, quantification limit, precision, linearity, and uncertainty) obtained in this experiment shown that this method can confidently be applied for the determination of certain elements (Ca, Mg, P, S) in the automotive engine oils. More elements also have the potential to be analyzed by this method.

Acknowledgment
The authors would like to show their gratitude to Ilham, Elva Istifani, and Indra Hadiwijaya for their support in preparing and analyzing lubricating oils used in this study. We thank B4T (Center for Material and Technical Product) for providing sample and testing laboratory. Special thanks delivered to LPDP for funding.

References
[1] A Wolak, Zajac G and Gołębiowski W 2019 Determination of the content of metals in used lubricating oils using AAS Pet. Sci. Technol. 37(1) 93–102
[2] Santos N D S A, Roso V R, and Faria M T C 2020 Review of engine journal bearing tribology in start-stop applications Eng. Fail. Anal. 108 104344
[3] Kemenperin 2018 Permenperin No.25 Tahun 2018
[4] Stan C, Andreescu C and Toma M 2018 Some aspects of the regeneration of used motor oil Procedia Manuf. 22 709–13
[5] Stout S A, Litman E and Blue D 2018 Metal concentrations in used engine oils: Relevance to site assessments of soils Environ. Forensics 19(3) 191–205
[6] Selby T W, Bosch R J and Fee D C 2005 Phosphorus additive chemistry and its effects on the phosphorus volatility of engine oils J. ASTM Int. 2(9) 153–68
[7] Brown S F 2015 Base oil groups: Manufacture, properties, and performance Tribol. Lubr. Technol. 71(4) 32–5
[8] Zali M A, Ahmad W K W, Retnam A and Catrina N 2015 Concentration of Heavy Metals in Virgin, Used, Recovered and Waste Oil: A Spectroscopic Study Procedia Environ. Sci. 30 201–04
[9] ASTM D4628-16 2016 Standard Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry ASTM Int. 05.02
[10] ASTM D5185-18 2018 Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) ASTM Int. 05.02 800–800–6
[11] ASTM D4047-00 2000 Standard Test Method for Phosphorus in Lubricating Oils and Additives by Quinoline (05) 1–4
[12] ASTM D4951-02 2008 Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry Man. Hydrocarb. Anal. 6th Ed. 05 766-766–5
[13] ASTM D1266-98(2003) 2008 Standard Test Method for Sulfur in Petroleum Products (High-Temperature Method) ASTM Int. 98 272-272–5
[14] ASTM D2622-03 2008 Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry ASTM Int. 05 402-402–4
[15] ASTM D6481-99(2004) 2010 Standard Test Method for Determination of Phosphorus, Sulfur, Calcium, and Zinc in Lubrication Oils by Energy Dispersive X-ray Fluorescence ASTM Int. 99 1–5
[16] ASTM D4294-16c1 2016 Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry ASTM Int. 05.02
[17] Fernández-Feal M 2018 Study of Metal Concentration in Lubricating Oil with Predictive Purposes Curr. J. Appl. Sci. Technol. 27(6) 1–12
[18] Gazulla M F, Orduña M, Vicente S and Rodrigo M 2013 Development of a WD-XRF analysis method of minor and trace elements in liquid petroleum products Fuel 108(March) 247–53
[19] BSN 2018 SNI ISO/IEC 17025:2017, Persyaratan umum kompetensi laboratorium pengujian dan laboratorium kalibrasi
[20] Shrivastava A and Gupta V 2011 Methods for the determination of limit of detection and limit of quantitation of the analytical methods Chronicles Young Sci. 2(1) 21
[21] Magnusson B and U Örnemark (eds.), 2014 Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics
[22] CIPAC 2003 Guidelines on method validation to be performed in support of analytical methods for agrochemical formulations 3807
[23] Rao, T N 2018 Validation of Analytical Methods Validation of Analytical Methods, Calibration and Validation of Analytical Methods - A Sampling of Current Approaches IntechOpen
[24] Markowicz A and Haselberger N 2004 Quantifying uncertainty in nuclear analytical measurements, XRF Analysis of Intermediate Thickness Samples IAEA-TECDOC-1401 July 37–8
[25] Fiamegos Y and de la Calle Guntiñas M B 2018 Validation strategy for an ed-xrf method to determine trace elements in a wide range of organic and inorganic matrices based on fulfilment of performance criteria Spectrochim. Acta - Part B At. Spectrosc. 150(July) 59–66
[26] Eurachem 2012 Quantifying Uncertainty in Analytical Measurements Third Ed. EURACHEM
[27] Sitko R and B Zawisza 2012 Quantification in X-Ray Fluorescence Spectrometry X-Ray Spectroscopy ed D S K Sharma (Ed. InTech)