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VERIFICATION AND USE OF CONTROL CHARTS IN SPECTROCHEMICAL ANALYSIS;ESTIMATING MEASUREMENT UNCERTAINTY

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Introduction: Consistency in analysis depends on being aware of a significant change in instrumental response, such as that caused by drift or changes in analytical precision, or both, and taking corrective action. The usual corrective action for drift is standardization. Standardization, however, when there is no real need, ca only broaden the spread of subsequent analyses. One purpose of this practice is to set guidelines that will avoid overstandardization.

To control manufacturing processes, there must be confidence that a consistent material is being produced and that the analysis of the material is reliable.

For assurance that the material meets specification, a purchaser may require the supporting record of control charts to assess that proper analytical control has been maintained..

Keywords: spectrochemical, measurement uncertainty, control charts

1. SULFUR IN PETROLEUM AND PETROLEUM PRODUCTS BY ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

1.1.Scope

This test method covers the measurement of sulfur in hydrocarbons, such as diesel, naphta, kerosene, jet fuels, crude oils, gasoline and other distillates.

1.2 Summary of Test Methode

The sample is placed in the beam emitted from an x-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standards that that bracket the sample concentration range of interest to obtain the sulfur concentration in mass %.

1.3.Instrument Configuration

Oxford Lab-X 3500 S is a dedicated sulphur analyser

Tube: 10 kV
Target: Ti
Detector; neon higher performance detector
Gas purge: He
Primary filters: W2
Secondary filters: not relevant

1.4. Accessories

- Liquid sample cells
- -secondary window stages
- Poly S – X-ray sufficiently transparent film – resist attack by the sample - free of sulphur

2. QUALITY CONTROL PROGRAM

2.1. Corection of interferences – Restandardisation

There are two main types of interference to be considered:

(i) Instrument imperfections (Overlaps due to insufficient resolution)
(ii) Matrix effects (due to large changes of matrix absorption)

In addition to these problems occurring between elements in the sample being measured, there can also be changes of spectral background affecting the measurement of elements in low concentracion. As a general rule, if it is necessary to measure below 1000 ppm it will be necessary to consider some form of background correction unless the overall matrix is quite constant.

The spectral background varies inversely with the average atomic number of the samples. That is to say higher the average atomic number (and mass absorption coefficient) of the sample, the lower the scattered background. This effect is also shown in the intensities measured from the scattered X-ray tube anode lines.

These characteristic lines are scattered from the sample and the lower the average atomic number of the sample the higher their intensities will be.

Scattered intensities are directly related to the spectral background and, if ,measured, can be used to make measured background corrections of other element gross peak intensities.

It can be seen that the simplest form of background correction is the subtraction of a fixed amount equal to I_o from each measured intensity, commonly referred to as ‘Blank Subtraction’. Such a procedure produces a series of net intensities related to concentration by;

$$C = a_1 * I$$

The principal use of this form of background correction is for the determination of silicone on paper.

A overlap correction can be applied to either a tube line or an overlapping element line. The corrected, or net, intensity (I^N) is calculated as follows:

$$I^N = I^{measured} - K * I^B$$

The value of K for a tube line is determined by measuring a ‘blank; base material. If measuring sulphur in a diesel oil, a suitable blank is a low viscosity mineral oil does not contain any sulphur.

Spectral overlaps are corrections in a similar way but here the special samples needed to calculate the correction factor must contain both a significant amount of the overlapping element and none of the analyte element present. Oxford supply Setting Up Sample (SUSs) which are suitable for this purpose.

SUSs are an essential part of quantitative analysis . During the initial calibration their measurement provides the sensitivity and background . Thereafter, whenever it is necessary a new measurement of them will allow the software to quantify any change in the instrument’s performance and apply a drift correction. This is the procedure for ‘ restandardisation’.

Restandardisation samples (SUSs) are special samples wich contains required element of interest in the requested region of calibration curve.

2.2. Calibration

General principles as Calibration - X-ray analysis , as with other forms of spectroscopy, is a comparative technique. This means it is necessary to have a series of reference standards which cover the element to be measured in the ranges of interest. These are measured and the intensities for the elements to be analysed are recorded so that calibrations of concentrations versus intensity can by derived and stored in the data processing computer for future analysis of unknown samples of the same type.

Before the standard samples can be measured it is necessary to decide the sample preparation methods that will be employed.

XRF analysis is a volume analysis; the depth of sample involved in the analysis depends greatly on the matrix material (ie:absorption) and the energy of the X-rays being measured.

The simplest form of calibration is a straight line , and this basic relationship between concentration and intensity is the sensivity of the instrument. The equation of the straight line is given by:

$$C = a_0 + a_1 * I_m$$

Such that the concentracion for an ‘unknown’ sample can be calculated by measuring the intensity from the instrument and using the a_0 and a_1 coefficients. This equation is derived from the following:

$$Y = mx + c$$

Were y is the intensity measured (Im), m is the sensitivity (Q) and c is I_0. The equation becomes:

$$I_m = (Q \times C) + I_0$$

Rearrangement of this gives:

$$C = I_m / Q - I_0 / Q$$

If $a_0 = -I_m / Q$ and $a_1 = 1/Q$ then the equation becomes:

$$C = a_0 + a_1 * I_m$$

The magnitude of the term a_0 , which is normally negative, is called the Background Equivalent Concentration commonly known as the BEC. It is possible to use an intensity intercept I_0, but this is less common.

The inverse of the slope term $1/a_1$ is equal to the *number of counts/seconds/unit* of concentracion used. This is referred to as Q in our documentation and will be used in formulae to express the precision of the instruments.

Precision – is used to describe the *repeatability of the instrument* , and to give it some numerical significance, it is normally described as the *standard deviation*.

Typical *Gaussian distribution* is used for measured value where random events are involved. The deviation from the mean value for approximately 66% of all the measured values is a number which is called *sigma.* Twice this value takes in 95 % of all the measured values and three times sigma 99.97% of all. These break-points are used frequently to describe various levels of confidence.

That is to say, there is a 1 in 20 chance in getting a result with a deviation larger than twice the one sigma value.

With X-ray analysis the measurements are made up of a series of numbers accumulated by counting photons of a particular energy entering a detector. This counting process obeys a Gaussian distribution and the standard deviation 1 sigma is equal to:

1 sigma = root of (total number of photons counted)

but

total number of photons counted = (C + BEC) x QT

where:

BEC = Background Equivalent Concentracion

Q = Sensitivity

T = Counting / analysis time

C = Concentracion

1 sigma = root of((C + BEC)xQT)counts

however:

QT counts = 1 %

So that :

1 sigma = root of((C+BEC)xQT) / QT %
1 sigma =root of(C+BEC)/QT %

From this it seen that:

Sigma at zero = root of BEC/QT %

Three times this value is known as the limit of detection LOD.

Accuracy – The terms ‘accuracy’ and ‘precision’ are often interchanged and wrongly used. The definition is, however, quite clear: *‘precision’* is the ability of the instrument to repeat a result from the same sample. Precision and time are intimately related. For example, if it required to improve the sigma at a particular concentracion level by a factor 2, then counting time must be increased by a factor of 4. That is to say, the time must increase by the square of the improvement required.

‘Accuracy ‘ is the *correctness* of result compared with other reference methods of analysis.
A useful way of expressing the accuracy is in terms of the *standard error* (standard deviation of differences between X-ray and given values) of the calibration curve.
From this, it follows that an instrument can have excellent precision or reproducibility but that the value being produced could be quite wrong. A classical cause for this would be a poor calibration, possibly caused by insufficient calibration standards, inaccurate concentracion values, errors in sample preparation, etc.
Standards are prepared from sulfur compound (di-n-bytil sulfide) of known sulfur content, and specific matrix diluent. The matrix diluent is to close to the form of the matrix being analysed . A diesel calibration is based on six diesel standards.

2.2. Validation

It is good practice to validate the calibrations, at least, once a year. For this purpose, certified reference materials are using.

2.3. Quality Control Samples (QCS)

QCS is independently prepared, stable reference material. The concentration of the QCS is near the expected concentration of the real samples being analysed. QCS is regularly tested as if they were unknown production samples. Results are recorded and immediately analysed by control Charts.

2.4. Control Charts (CC)-Steps of Preparing

Calculating the standard deviatin of the measurement (s_0).
Drawing a horizontal line for the calculated average measurement of the verifier, X_0, and marking central line *CL*.
Calculating the upper and lower control limits; 3-sigma limits, using the following two equations:

$$UCL_x = X_0 + As_0$$
$$LCL_x = X_0 - As_0$$

Where
**A*= factor for Computing Control Chart Lines for *n o*bservation
And
S_0 = established standard deviation of a measurements.
Drawing horizontal lines for these, and marking UCL and LCL.

.Plotting- As data is obtained for a verifier, show a record of standardized readings with calculations of average, UCL and LCL.
Including data and time as well as notations on what corrective action was taken or what extraordinary conditions prevailed at specified times.

2.5.Corrective Action

Restandardisation is made occasionally, depending on the stability of the enviroment, instrument itself and required precision. This may warry from 8 hours period up to 1-2 months cycle. The good practice is daily checking performance, using the QCS and analysing one of the SUSs. Purpose of the QCS is to prove the accuracy of the calibration curve, and SUS is used to prove stability of the equipment. We have the graph with control lines, where can see concentracion versus time, where SUS value, recorded at the time of calibration, represents 'original value' for the day 'zero'. Then every day before routine analysis, instrument is confirmed by measuring SUS, which result is then put into the graph. If the obtained value is higher or lower then allowed limits, restandardisation is necessary. On the other hand if the value is within limits, we can proceed to the next step to analyze QCS. SU-S20B content 0.85 % mass of sulphur; 'Higher allowed limit' for SU-S20B is 0.935 % mass, and lower allowed limits is 0.765 % mass. For 'Low SUS we use liquid sample for better matrix correction. This SUS should not contain measured element (or very little).In Ours cases, it is specific matrix diluent .

Restandardistion has to be performed in the following cases:

- after replacing helium grade
- after regular service
- after exchanging XRF film supplier
- when changing QCS material
- in case of claim process
- after each new calibration.

In the following cases Restandardisation will probably not help and *calibration* will be required:

- replacing of the crucial part of the instrument (crystal, detector, X-ray tube, preamplifier, HV supply for detector or XRT, I/Oboard ect.)
- new concentracion range of interest (lower S)
- if the matrix of the sample tremendously change because of the different process (e.g. if new additive is used K or Mn in gasoline…)

If the Restandardisation is not successful, the new calibration has to be made. Sometimes, it is easier to make new calibration, because XRF equipment is stable enough to be restandardised 2-3 times per year.

CC - No action is required if measurements are within 2-sigma of the CL line.

Option before undertaking a restandardization / calibration:

Check that the spectrometer is correctly profiled and repeat the verification.

Even if the profile did not require correction, reburn the verifier and average readings with the earlier test. Multiply the overall average and plot this as a data point. Standardize only if the new data point still plots beyond the UCL or LCL line.

Make a halfway restandardization, if possible, when four out of five successive data points fall more than 1-sigma from the CL line.

2.6. Estimating Measurement Uncertainty

Horwitz (3), Thompson and Lowthian (4) have published generalised models relating the coefficient observed in an interlaboratory study to the concentration of analyte. The within-laboratory standard deviation observed for the matrix-spiked controls was multiplied by three to approximate a 95 % confidence interval.

3. PERFORMANCE

TABLE I . Calibration performance

Range (Sppm)	Counting Time (sec)	Accuracy Std. error (S ppm)	*TLOD (S ppm)	*GLOD (S ppm)	Precision (95% Confid.)
7-1000	200	8	5	7	4
1-5000	100	8	7	10	8

Where are:

**TLOD* = Theoretical limit of detection
**GLOD* = Guaranteed limit of detection

TABLE II. Validation data

Sulphur NISTstandard	Certified conc.(%mass)	Measured conc (%mass)	Error (%mass)
1616a	0.0146	0.0144	-0.0002
1617a	0.1731	0.1750	+0.0019
2724a	0.0430	0.0410	-0.0020
2717	3.022	3.003	-0.018

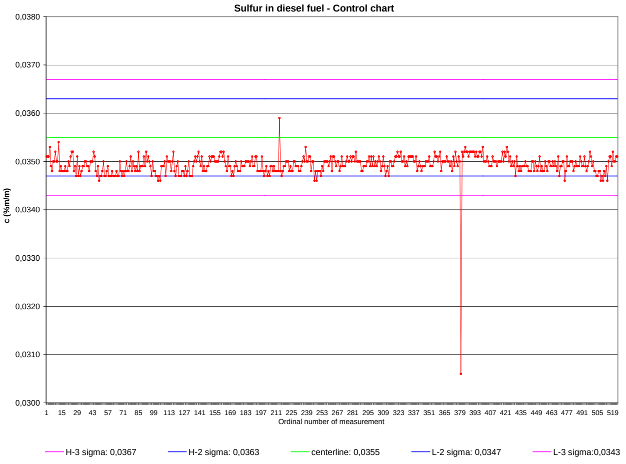

Fig.1. Control Chart – Sulfur in Diesel Fuel

TABLE III. Uncertaionty

Sulfur concentration , % mass	0.0355
Standard Deviation S_0 , % mass	0.0004
Uncertainty, *U (k=2),* % mass	$3xS_0$ (from CC) =0.0012

4. CONCLUSION

This practice covers procedures for determining if a spectrochemical analysis is under statistical control.

Criteria are presented for determining when corrective action is required.

Control will be effected by using verifiers to test instrument response. It is recommended, although not required, that this be accompanied by the plotting of control charts.

Limitation The procedures that are described do not apply to analysis that require a calibration each time a set of analysis is run (for example, Atomic Absorption Spectrometry !).

For robustness system (X-ray Spectrometers!), this practice offer very simple method for estimating measurement uncertainty.

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