The Estimation of Uncertainty by the Utilization of Validation and Quality Control Data; Lead in Gasoline by AAS

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Abstract-This protocol was developed to estimate the uncertainty of measurement of a chemical analysis by utilizing in-house validation studies and quality control data. The approach was to generate an estimate of the uncertainty across the analytical concentracion range. This was to be expressed as a mathematical equation or factor that could be inserted into a Laboratory Information Management System (LIMS) and thus produce an uncertainty estimate from an entered analytical result .

The aim is to identify as many sources of uncertainty as possible and account for them by appropriatte precision and trueness studies. Any additional sources of uncertainty are evaluated by other means such as calibration certificates, published dana, etc.. It is not necessary to evaluate every source of uncertainty if they are deemed insignificant, unless there are a large number of them. Uncertainty components that are less than one third of the largest component are not evaluated in detail. A preliminary estimate of the contribution of each component or combination of components to the uncertainty is made and those that are not significant eliminated . The uncertainty contributions is expressed as standard deviation, and combined according to the appropriate rules, to give a combined standard uncertainty. Coverage factor (2 for normal distribution) is applied to give an expanded uncertainty.

I. The Test Method

A. Analysis Principle

The gasoline sample is diluted with 2-propanol, and the alkyl lead components are stabilized by reaction with iodine and a quaternary ammonium salz. The lead content of the sample is determined by atomic absorption flame spectrometry at 283.3 nm, using standards prepared from reagent grade lead chloride. By the use of this treatment, all alkyl compounds give identical response. This test method is used to ensure compliance of trace lead for lead-free gasoline.

B. The Standards Preparation

Stock lead solution, c (Pb) = 10mg, as chloride; commercially available Standard.

Organic standard solution, c (Pb) = 100 mg/l – dilute 10 mg stock lead solution to 100 ml with propan -2-ol, in a volumetric flask. Solution is stable for a least 6 mounths.

Preparation of a set of calibration standards - preparing calibration solutions with a lead content of 0.5, 1.0, 1.5, 2.0 and 2.5 mg/l as follow.

Using a calibrated pipette, transfer 0.5, 1.0, 1.5, 2.0 and 2.5 ml organic standard solution into a series of five 100 ml one mark volumetric flaskseach containing approximately 50 ml of propan-2-ol and 10 ml of a mixure of 50 % (v/v) of toluene and 50 %(v/v) iso-octane. Add 1ml of iodine solution , agitate and allow to standard for 1 minute. Add 5 ml of methyltrioctylammonium chloride solution, and dilute to the mark with propan-2-ol.

C. Sample Preparation

Transfer approximately 50 ml of propan-2-ol into a volumetric flask and add 10 ml of the sample by means of a pipette, using the suction ball. Add 1 ml of the iodine solution, agitate and allow to stand for 1 minute. Add 5 ml of the methyltrioctylammonium chloride solution and dilute to the mark with propan-2-ol.

If less than 10 ml of sample are used, make up the volume to 10 ml using the mixure of 50 % (v/v) toluene and 50 % (v/v) iso-octane.

D. Assumption

1. The sample is considered homogeneous and any uncertainty due to deviation from homogeneity can be considered small in comparision to other uncertainties calculated
2. The chemistry is relatively similar between samples. The samples are pre-treated with iodine, and lead-alkil-compounds are stabilisated with quaternar salz.
3. The uncertainty of the standard curve was not included in the uncertainty determination because the variation of the absorbance within days and between days is included in the estimate of the uncertainty of the QC sample.

II.Calculation of Uncertainty

A. Preliminary Study of Compounds Type B – " sources of random errors"

Standards

The commercially available Pb Standard solution has a manufacturer's stated uncertainty ± 0.2 mg . The value of the uncertainty is given without a confidence level or distribution information, so an assumption is necessary. Without any other information a rectangular distribution is assumed and therefore the semirange is divided by √3.

$$U_{stock} = 0.2 / \sqrt{3}$$
$$= 0.01156 \text{ mg}$$

Pipetter

Manufacturer's specification: Tolerance = max. ± 0.03 ml

Certificate of Verification : Standard error < 0.03 ml – a triangular distribution is assumed and therefore the semirange is divided by √6.

$$U_{pip} = 0.03 / \sqrt{6}$$

$$= 0.01229 \text{ ml}$$

Volumetric flask

Manufacturer's specification： Tolerance = ± 0.1 ml

Certificate of Verification : Standard error = 0.04 ml – a triangular distribution is assumed and therefore the semirange is divided by √6.

$$U_{flask} = 0.04 / \sqrt{6}$$

$$= 0.0163 \text{ ml}$$

Temperature – the difference between the laboratory temperature and the calibration temperature

The volumetric flask is calibrated at a temperature of 20 ^{o} C, however, the laboratory temperature varies between the limits of ± 5 ^{o} C. The uncertainty from this effect can be calculated from estimate of the temperature range and thecoefficient of the volume expansion. The coefficient of volume expansion for propan-2-ol is 1.016 x 10^{-3}ml ^{o} $C^{-1.}$

$$^{U}{}_{temp} = V\ x\ Temp\ x\ Coefficient\ of\ Expansion\ propan\text{-}2\text{-}ol$$

$$= 100\ x\ 5\ x\ 1.016\ \mathrm{x}\ 10^{-3}\mathrm{ml}\ ^{o}\ \mathrm{C}^{-1.}$$

$$= 0.505\ ml$$

Convert to the standard uncertainty and assume rectangular distribution

$$^{U}{}_{temp} = 0.505 / \sqrt{3}$$

$$^{U}{}_{temp} = 0.290\ ml$$

The combined uncertainty of the volumetric flask is:

$$U\ volumetric = \sqrt{(\ U_{flask}\ )^{2} + (^{U}{}_{temp})^{2}}$$

$$= 0.29\ ml$$

The combined uncertainty of standards is:

$$U_{std} = c_{std}\ x\ \sqrt{(U_{stock}\ /conc)^{2} + (\ U_{pip}/pip)^{2} + (U\ volumetric/vol)^{2}}$$

$$U_{std} = c_{std}\ x\ 0.023\ mg/l$$

III The Method Validataion - compounents type A– statistical parameters

Intermediate Precission - Validation Procedure is establish the effects of random events on the precision of analytical procedure. Quality control material is analysed by different analysts, and by different technique.

Analyst	**Lead concentracion, mg/l**
1.	13.1
	13.2
	13.1
2.	13.5
	13.7
	13.5
3.	13.7
	13.7
	13.7
Average	**13.3 mg/l**
SD_{IMP}	**0.339 mg/l**
RSD	**2.5 %**

Accuracy/Trueness - Validation Procedure is establish the closeness of agreement between the value which is accepted either as an reference value and the value found.

CRM – NIST SRM ; c_{ref} (Pb) = 7. 9 ± 0. 3 mg / l

Measurement No.	c_{meas} (Pb) , mg/l	Recovery %	RSD %	SD, mg/l
1	7.6	96	3.6	0.3
2	8.2	103	1.0	0.3
3	8.1	102	2.5	0.2
4	8.2	103	2.7	0.3
5	8.2	103	1.9	0.3
6	8.3	105	0.4	0.4
Average:	**8.1**	**102**	**2.0**	**0.3**

Working / calibration standards:

c_{ref} (Pb) , mg / l	c_{meas} (Pb) , mg /l	Recovery %	RSD %	SD, mg/l
0.5	0.550	110	4.4	0.0242
0.5	0.531	106	0.7	0.00372
0.5	0.535	107	4.3	0.0230
1.0	1.043	104	2.9	0.0302
1.0	1.063	106	1.1	0.0100
1.0	1.063	106	1.9	0.0200
2.0	2.025	101	0.8	0.0016
2.0	2.004	100	0.9	0.0018
2.0	2.020	101	1.3	0.0026
10	10.10	101	3.3	0.3300
10	10.18	102	0.4	0.0400
10	10.01	100	0.9	0.0900
15	14.40	96	0.4	0.0580
15	14.55	97	0.8	0.1200
15	14.67	98	1.4	0.2100
25	29.64	102	1.6	0.400
25	29.39	101	2.1	0.530

25	103	1.7	0.4400
30	99	0.5	0.1500
30	99	0.6	0.1800
30	98	2.8	0.8200
Recovery Average	**102 %**	**$SD_{accurecy}$ = 0.16 mg / l**	

IV Combined Uncertainty

The measurement system is under statistical control. The components type B are " covered" with statistical parameters.In the case of the unsatisfactory precision or accurecy, must be made revalidation . Combined Uncertainty is calculated by combining an uncertainty of the intermediate precision , with combining uncertainty of the trueness

$$U_{com} = \surd\,(SD_{IMP})^2 + (SD_{accurecy})^2$$

$$U_{com} = 0.37\ mg / l$$

V Expanded Uncertainty

Coverage factor (2 for normal distribution) is applied to give an expanded uncertainty.

$$U_{exp} = 0.74\ mg / l$$

VI. Conclusions

This approach was developed to be applicable to ‘’calibration chemistry’’ and not ‘’stochiometric chemistry’’ as ‘’calibration chemistry’’ is greather than 95% of the analysis performed in our laboratory. Calibration chemistry is based on having a standard and making a calibration curve with it, then isolating the analyte, and quantifying the analyte agains that curve.

References

[1] EURACHEM/CITAC (1995) Guide Quantifying uncertainty in analytical measurement
[2] EN 237(1996) Liquid petroleum product- petrol- Determination ol low lead concentrations by atomic absorption spectrometry .