

Quality Control Assessment for Chemical Analysis

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Abstract: *The current research focused on the importance of quality control for chemical analysis through instrument calibration conditions, on different organochlorine pesticides samples using standard mixture solutions. For this aim statistical quality control calculations were performed to optimize the validation of Gas chromatography mass spectrometry (GC-MS) and its compatibility range. The obtained quality control assessment results confirmed instrument method's performance in term of the instrument accuracy, excellent sensitivity and selectivity of the consequences.*

Keywords: Quality control, Chemical analysis, Lower detection limit.

1. Introduction

Quality has become a crucial demand in the social, economic, technical and scientific field. Despite the fact that the concept is as old as human activities, it has become a buzzword in the last few years. One of the important things that should consider during analysis is the calibration and that any calibration expression is adequate, important statistics-related questions must be asked. It should be noted that although all of the following questions are important, perhaps the most important (and often neglected) query is the last one regarding uncertainty [9].

- 1) Was the design of the calibration study appropriate?
- 2) Were the resulting data analyzed in a statistically sound manner?
- (2a) Is the chosen model adequate?
- (2b) Is the fitting technique appropriate?
- (2c) How much bias does the curve reflect?
- (2d) What is the uncertainty in any sample result that is estimated from the curve?

Therefore, it is important to choose the correct calibration model for each particular analyte even though this could prove to be time consuming, particularly when establishing a new method for over a hundred analysts [2], [3]. The unwise choice of a calibration model may give rise to inaccuracies as high as 100% for analytical determinations due to the presence of high random errors and bias [9]. Statistical calculations and distributions therefore, play a major role in performing validation in chemical measurements and analytical determinations as well as systematically determining the level of certainty reached by the analytical procedure [9].

Statistical designs are required to test whether the correct calibration design was chosen, whether the data fit the model precisely, identify outliers as well as determining the level of bias contributed on each analytical system, component or module of the measurement system (GC-MS). It is reasonable to expect that outliers will be present in analysis of matrix based extracts [4].

Generally, quality control assessment using GC Ms spectroscopy techniques on different organochlorine

compounds is very important. The Organochlorine pesticides (OCPs) are a kind of widely used pesticides for the effective control of pests and diseases of plants and animals [1]. Due to its low biodegradability and high persistence in the natural environment, OCPs is ubiquitous among samples of air, water, soil, sediments, food, and biological tissues and has been shown to have potentially harmful effects on human beings. Some OCPs, including hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs), aldrin, dieldrin, endrin, chlordane, heptachlor, and hexachlorobenzene, are listed in the Stockholm Convention as persistent organic pollutants (POPs) and have been banned by the United Nations Environment Program (UNEP) for their link to reproductive disorders, disruption of the cellular immune system, cancer predisposition, and nervous system damage of humans [5]– [11].

2. Experimental

2.1 Materials

For this study, different types of organochlorine residues were considered for the quality control study as provided in Table 1.

Table 1: Reference material for the organochlorine compounds

Compound name	Purity (%)
HCH-alpha	99.0
HCH-Beta	99.0
HCH-gamma	99.0
Heptachlor	99.0
Aldrin	98.0
Heptachlorepoxyde	98.0
2,4 DDE	99.0
Endsulphane - alpha	98.0
di-aldrin	98.0
2,4 DDD	99.0
Endrin	98.0
Endsulphane-beta	96.0
4,4 DDD	99.0
2,4 DDT	99.0
4,4 DDT	99.0

2.2 GC-MS instrument configuration

Characterization of different pesticides residue were injected to GC MS spectroscopy and the analytical spectra were done by an Agilent Technologies 6890 GC, coupled to an Agilent Technologies 5975 Quadrupole. Mass Selective Detector was used for analysis using, a 30 m x 0.25 mm x 0.25 μ m DB-5 MS column with stationary phase 5% vinyl and 95% dimethylpolysiloxane. The GC-MS system utilised a 5 with an injector temperature of 25 °C and a Gerstel auto sampler delivering 2 μ L L injection volumes at an injection speed of 50 μ L s⁻¹ and splitless mode with a purge valve time of 50 s. Total runtime for the analysis was 37.32 min with initial temperature of 50 °C and hold time of 2 min. and ramp 1 at 25 °C min⁻¹ to 160 °C, with no hold time, followed by ramp 2 at 3 °C min⁻¹ with no hold time and ramp 3 at 8 °C min⁻¹ to 270 °C with no hold time with a solvent delay of 4.5 min. A constant pressure of 135 kPa was maintained with an average linear velocity of 50 cm s⁻¹.

3. Results and Discussions

3.1 Statistical Evaluation of the Results (Repeatability)

There are many factors that affect the ability of results including: poor instrument quality, instruments out of calibration, inadequate methods of data collection and operator inefficiency or inexperience. Hence, was carried on a repeatability test, for better results correlations

Table 2: Instrument repeatability using pesticide residue standard mixture (0.05 mg/L)

Compound name	Repeatability of Peaks area		
	1 st injection	2 nd injection	2 nd injection
HCH-alpha	62700	63702	61968
HCH-Beta	79470	78146	79532
HCH-gamma	16728	17505	16698
Heptachlor	19726	18910	19112
Aldrin	3608	3492	3303
Heptachlorepoxide	10028	10793	10167
2,4 DDE	3608	3492	3303
Endsulphane - alpha	9707	9371	9338
di-aldrin	3785	3479	3573
2,4 DDD	7377	7638	7787
Endrin	22456	22608	21717
Endsulphane-beta	1522	1569	1661
4,4 DDD	6223	6133	5861
2,4 DDT	52057	50101	48893
4,4 DDT	24850	24207	24356
HCH-alpha	14285	15234	15142

When conducting repeated measurements for collecting data such as in this study, shrinkage of the correlation coefficients inevitably occurs. In this study, the use of multiple regression models was avoided and a classical linear regression was used for all organochlorine compounds. Shrinkage can be defined as the decrease in correlation coefficients of a calibration obtained from one data set compared to correlation coefficients of other data sets. To test the instrument repeatability, it was injected three times the standard mixture pesticide residue (0.05 mg/L). Table 3.

Instrument repeatability using pesticide residue standard mixture (0.05 mg/L). The achieved peak areas from the successive GCMS measurements show a close repeatability of the results, under same instrumental analysis conditions.

Moreover, results for real mean peak area, standard deviation of peak areas and relative standard deviation (RSD %), from injected standard mixture. 0.04 p.p.m. presented in table 2.

Table 3: Calculated results for each compound using standard mixture (0.04 p.p.m)

Compound name	Real mean peak area	Stand. Dev. of peak areas	RSD %	t-distribution (t _{0.95})
HCH-alpha	62790	870	1.39	4.30
HCH-Beta	49049	783	0.99	4.28
HCH-gamma	16977	458	2.69	4.30
Heptachlor	19249	425	2.21	4.30
Aldrin	6191	108	1.74	4.30
Heptachlorepoxide	10329	408	3.95	3.27
2,4 DDE	3467	154	4.44	4.30
Endsulphane - alpha	9472	204	2.16	4.31
di-aldrin	3612	157	4.34	4.30
2,4 DDD	7600	207	2.73	4.30
Endrin	22260	476	2.14	4.30
Endsulphane-beta	1584	78	4.46	4.30
4,4 DDD	6072	188	3.10	4.30
2,4 DDT	50350	1596	3.17	4.30
4,4 DDT	2447	336	1.38	4.30
HCH-alpha	14887	523	3.52	4.30

3.2 Instrument detection limit

The instrument detection limit is the lowest detection above equipment, electronic signal noise. To set the lower detection limit, different concentrations of standard mixtures injected to GC-MS (0.08, 0.06, 0.04, 0.02, 0.01, and 0.005) p.p.m.

Figure 1, represents an example of an appropriate correlation between peak intensities, using different concentrations of pesticide residue standard mixtures.

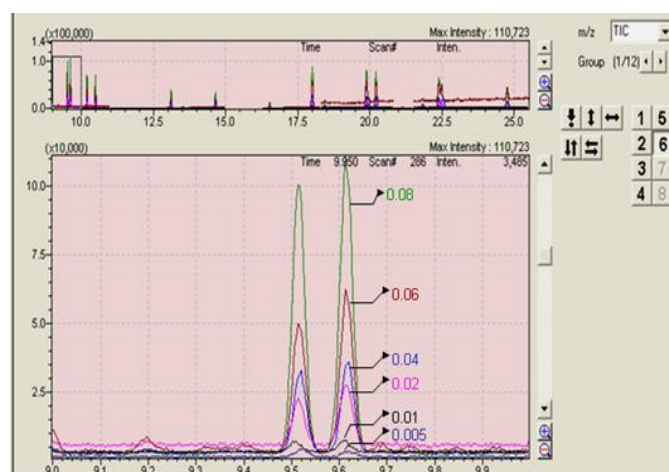


Figure 1: Peak intensities using different concentrations of pesticide residue standard mixtures.

3.3. Limit of Quantitation (LoQ)

Limit of quantitation (LoQ) is the lowest analyte concentration of spiked samples. In this validation study LoQ was performed on two examples and evaluated by multiplying with 5 calculated the standard deviation of the compound plus a concentration of lowest peak area of the blank. Recovery sample with spiked amount 0.05 p.p.m and other second recovery sample spiked 0.02 p.p.m, both results presented in table (4). The fraction of analyte added to a test sample (fortified or spiked sample) prior to analysis and percent recovery (%R) is computed as follows:

$$R (\%) = [(CF-CU) / CA] \times 100$$

CF is the concentration of analyte measured in the spiked sample. CU is the concentration of analyte measured in the unfortified sample while, CA is the concentration of analyte added (measured value) in fortified sample.

The LoD and LoQ were calculated as follows:

Limit of detection (LoD) = average concentration + 3 SD
 Limit of quantitation (LoQ) = average concentration + 5 SD

Table 4: Limit of quantitation for organochlorine pesticides (spiked amount 0.05 p.p.m, and 0.02 p.p.m)

Compound name	LoQ (0.05 p.p.m)	LoQ (0.02 p.p.m)
HCH-alpha	0.012	0.021
HCH-Beta	0.012	0.015
HCH-gamma	0.012	0.023
Heptachlor	0.016	0.021
Aldrin	0.011	0.014
Heptachlorepoxyde	0.011	0.03
2,4 DDE	0.023	0.01
Endsulphane - alpha	0.036	0.025
di-aldrin	0.026	0.014
2,4 DDD	0.019	0.023
Endrin	0.022	0.025
Endsulphane-beta	0.048	0.03
4,4 DDD	0.046	0.023
2,4 DDT	0.03	0.017
4,4 DDT	0.024	0.012
HCH-alpha	0.026	0.03

4. Conclusions

The instrument method calibration generating good results using standard mixture solutions over different samples concentrations. The Lower limit of detection (LoQ: 0.02 p.p.m and 0.05 p.p.m) was acceptable for all organochlorine pesticides. Moreover, the relative standard deviation (RSD%) is reported and ranges between 0.99 for HCB and the highest was for 4,4 DDT.

Previously, the obtained quality control results confirmed instrument method's performance in term of the instrument accuracy, excellent sensitivity and selectivity of the consequences.

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