

Atomic absorption spectroscopy for the determination of heavy metals in polyethylene moulding materials using Anderson–Darling statistics and top-down uncertainty estimates

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Abstract: Quality control data of heavy metal content (in terms of Pb) detected by atomic absorption spectroscopy in moulded polyethylene packaging material were analysed. A hypothesis of normal distribution was accepted at the 95% confidence level. Established individual and moving range charts indicated that $\approx 99.7\%$ of all normally distributed data fell within expected limits, assuming that the variability of the measurement system was due to random error. The atomic absorption spectroscopy system under investigation could not be considered suspect as neither the Anderson–Darling test nor the other analysis failed. Further, to monitor trends in the average, an exponentially weighted moving average line was overlaid on the ‘individual’ chart to enhance its sensitivity in detecting deviations. Based on long-term experimental data and statistical analysis, the atomic absorption spectroscopy system was assumed to be reliable with negligible bias, and a Pb content of 0.014 mgL^{-1} proposed for in-house reference.

Introduction

This paper provides information on the determination of heavy metal content in quality control (QC) samples of moulded polyethylene packaging material by atomic absorption spectroscopy (AAS), under intermediate statistical control conditions^[1–4].

Materials for QC are stored as a homogeneous bulk with similar composition to the test samples usually used for AAS. Specific samples are routinely taken from the bulk for QC of the AAS system, under intermediate conditions^[5–8].

To test the QC samples, the Anderson–Darling technique is used first to check that the calibration function is linear, under a model of constant residual variance, and then to test the performance of the recalibrated AAS system. It is recommended that an individual chart is overlaid with an exponentially weighted moving average and that a moving range chart is used to monitor the validity of the calibration curve when the function has been used for an extended period of time. The Anderson–Darling technique can be adapted to demonstrate the continuous proficiency of AAS analytical measurement systems that are used for QC measurements and indicate areas of potential measurement system improvement, and are also useful for evaluating uncertainties of measurement systems in statistical analysis^[9–11].

In combining standard uncertainties, the bottom-up approach outlined in the Guide to the Expression of Uncertainty in Measurement (GUM)^[12] and the Anderson–Darling technique (which is a top-down approach) are available. This study shows that the Anderson–Darling technique is simpler and more direct than the GUM approach. Thus, the AD technique appears to be more convenient and preferable in applications, especially for QC.

Experimental methods

Instruments and reagents

Atomic absorption spectrometer (Thermo Fisher scientific, model no ICE3000), thermostatic drum wind drying oven (Shanghai Precision Macro Experiment Equipment Co., model no DHG-9023A), polyethylene moulding product, pure acetic acid (analytical reagent grade), nitric acid (analytical reagent grade), distilled water, plastic food wrap.

Method

Food preservative film manufactured from the polyethylene moulding product was processed and then soaked in 4%(vol./vol.) acetic acid solution, at an ambient temperature of 60 °C for 2 hours followed by soaking in the appropriate liquid^[13,14]. Blank tests were also conducted, as controls. The instrumental parameters used to determine heavy metal (Pb) content in the soaking liquid^[15], by flame AAS, are shown in Table 1.

Table 1 Instrumental parameters for flame AAS

<i>Condition</i>	<i>Parameter</i>
Wavelength (nm)	217.0
Lamp current (%)	75
Pass band (nm)	0.5
Flame type	Air-C ₂ H ₂
Gas flow (L/min)	1.1
Burner height (mm)	7.0

Standard curve

A standard solution of 1000 mg/L Pb was used to create a standard calibration curve^[16]. The calibration curve was determined using serial dilutions (0.0, 0.5, 1.0 and 2 mgL⁻¹ Pb), as shown in Table 2. The curve fits the quadratic equation $y = 0.000037x^2 + 0.06994x + 0.0116$, where y is absorption intensity and x is concentration.

Table 2 Standard curve results

<i>Serial number</i>	<i>Concentration (mgL⁻¹)</i>	<i>Absorption</i>	<i>Fitting function</i>
1	0.0	0.012	
2	0.5	0.047	$y = 0.000037x^2 + 0.06994x + 0.0116$
3	1.0	0.081	
4	2.0	0.152	

Materials for quality control

A stable and homogeneous material with chemical properties similar to those of routine samples analysed using the AAS system was selected. The quantity of material required for each sample batch to be tested was estimated. Samples for QC were stored as appropriate for the specific AAS system, to ensure that all sample analyses of samples from a given batch were performed on essentially identical material.

Results and discussion

The QC sample from a specific batch was repeatedly analysed ($n = 20$) under intermediate conditions, in the AAS system (see Table 3). It is necessary to establish a protocol that all persons who routinely operate the AAS system should participate in the QC test. The results shown in Table 3 were obtained by testing the QC sample at random times over the normal period of AAS system operation, without special treatment, so as to obtain a more natural result, thereby minimising test bias.

Table 3 Quality control sample results	
Order, n	Result (mgL⁻¹)
1	0.0150
2	0.0192
3	0.0174
4	0.0122
5	0.0124
6	0.0189
7	0.0103
8	0.0160
9	0.0116
10	0.0185
11	0.0170
12	0.0140
13	0.0119
14	0.0118
15	0.0127
16	0.0144
17	0.0128
18	0.0139
19	0.0131
20	0.0152
Average	0.01442
Standard deviation	0.002650

The results of Table 3 were plotted sequentially to produce a run chart (see Figure 1), to screen data for any unusual patterns. Such phenomena as same-side continuous trends, abnormal clusters or cycles were not observed. If possible, such phenomena should be eliminated promptly as they are discovered. Next, Anderson–Darling statistics were used as an objective test for prior normality, in which variables based on the calculation examples of w standards are converted to normal cumulative probability P (shown in Table 4), finally obtaining $A^2 = 0.485$ and $A^{*2} = 0.506$. Since this value is less than 0.752, it indicates that the hypothesis of normal is accepted at the 95% confidence level for the measurements given in Table 3^[17,18].

Figure 1 Run chart

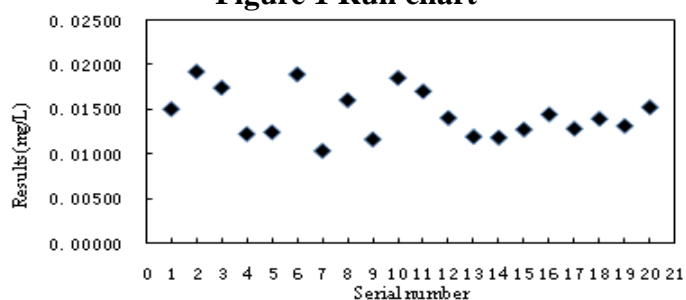
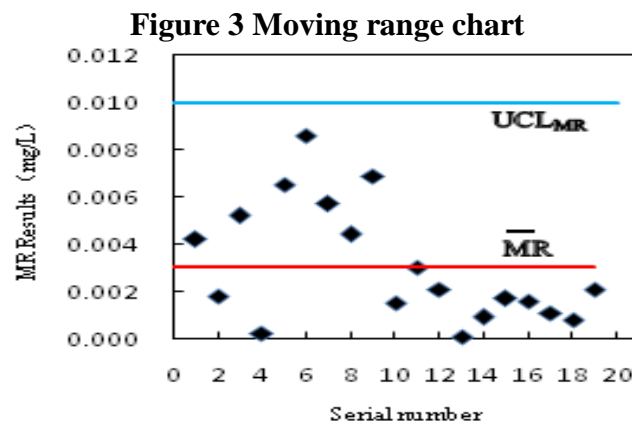
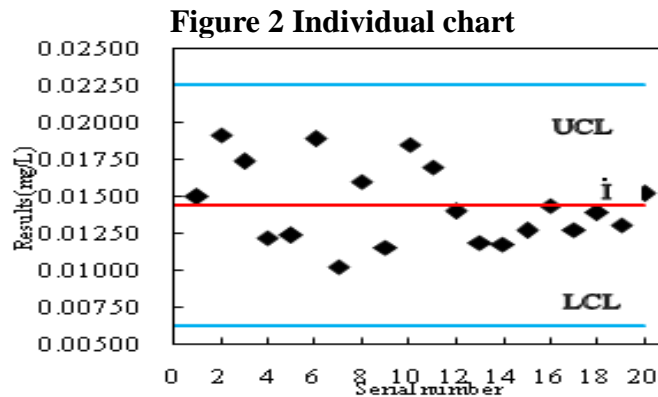


Table 4 Anderson–Darling statistics

Data	0.0150	0.0192	0.0174	0.0122	0.0124	0.0189	0.0103	0.0160	0.0116	0.0185
MR	...	0.0042	0.0018	0.0052	0.0002	0.0065	0.0086	0.0057	0.0044	0.0069
Ascending	0.0103	0.0116	0.0118	0.0119	0.0122	0.0124	0.0127	0.0128	0.0131	0.0139
w	-1.55	-1.06	-0.99	-0.95	-0.84	-0.76	-0.65	-0.61	-0.50	-0.19
P	0.0606	0.1446	0.1611	0.1711	0.2005	0.2236	0.2578	0.2709	0.3085	0.4247
A_i	-6.153	-15.07	-23.04	-26.68	-30.76	-30.70	-30.12	-32.85	-31.64	-27.16
		1	8	3	1	6	9	8	1	6
Data	0.0170	0.0140	0.0119	0.0118	0.0127	0.0144	0.0128	0.0139	0.0131	0.0152
MR	0.0015	0.0030	0.0021	0.0001	0.0009	0.0017	0.0016	0.0011	0.0008	0.0021
Ascending	0.0140	0.0144	0.0150	0.0152	0.0160	0.0170	0.0174	0.0185	0.0189	0.0192
w	-0.16	-0.01	0.22	0.30	0.60	0.98	1.13	1.54	1.69	1.81
P	0.4364	0.496	0.5871	0.6179	0.7257	0.8365	0.8708	0.9382	0.9545	0.9649
A_i	-29.02	-24.61	-21.21	-21.04	-16.63	-12.47	-10.75	-8.381	-7.502	-3.832
	3	2	3	8	7	1	8			
A²	0.485									
A^{*2}	0.506									

The individual and moving range charts can only be considered if the data are normally distributed. First, the individual chart (Figure 2), based on the data in Table 3, with its control limits and center line, was added to the run chart of Figure 1. In which, we cannot find indications of an out-of-control system, as well as one of the run rule strategy. Second, moving range methods were used to estimate the variance (see Figure 3).



In Figures 2 and 3,
the upper control limit is:

$$UCL = \bar{I} + 2.66\overline{MR} = 0.01442 + 2.66 \times 0.00307 = 0.0226$$

The lower control limit is:

$$LCL = \bar{I} - 2.66\overline{MR} = 0.01442 - 2.66 \times 0.00307 = 0.00624$$

and $\overline{MR} = 0.00307$ gives $UCL_{MR} = 3.27\overline{MR} = 3.27 \times 0.00307 = 0.01$

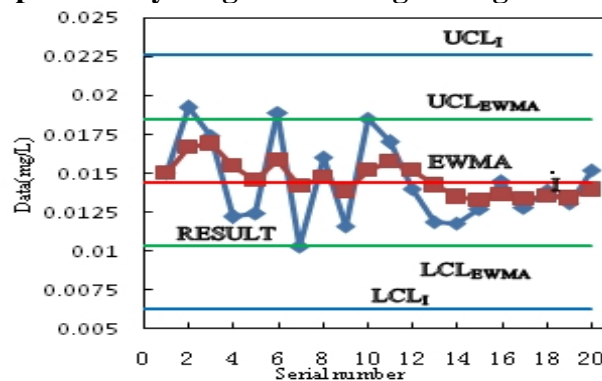
To further monitor the sensitivity in detecting the mean (Table 5), an exponentially weighted moving average trend line was calculated, using the recommended value of $\lambda = 0.4$. This trend line, with the following control limits, was overlaid on the individual chart (see Figure 4):

$$UCL_I = \bar{I} + 3s \sqrt{\frac{I}{2-I}} = 0.01422 + 0.00818 \times 0.5 = 0.0185$$

$$LCL_I = \bar{I} - 3s \sqrt{\frac{I}{2-I}} = 0.01422 - 0.00818 \times 0.5 = 0.0103$$

In Figure 4, similarly, there is no sign of change using any of these four strategies. Nor is there any evidence for the violation of run rules during operation of the measurement system.

Figure 4 Exponentially weighted moving average trend line overlay



As bias is monitored less frequently, batch QC testing is used to demonstrate the stability and uncertainty of the AAS system between bias tests. Nevertheless, considering the large quantity of quality data from the same batch being QC tested over a long period, and the previous regular performance of the AAS system, we finally take a value of 0.014 mgL^{-1} heavy metals in samples for its in-house reference, and set the t test for accuracy of the measurement system as:

$$t_{MR} = \frac{\sqrt{n}(\bar{I} - I_0)}{\overline{MR} / 1.128} = 0.673 < t_{0.975}(19) = 2.093$$

Where I is individual, I_0 is assumed to be zero, and $\overline{MR} / 1.128 = 0.00272 \approx 0.003$ is regarded as the current value of the standard uncertainty. Therefore, we accept the reliability and validity of the AAS system in determining the content of heavy metals in polyethylene moulding materials, and conclude that by maximising the combination of the effects on various variances from the techniques of \overline{MR} and of the pooled statistical dynamic monitoring described in this paper, it is possible to avoid the relatively complicated process of bottom-up methods of uncertainty evaluation ($u = 0.003$).

Conclusions

Anderson–Darling techniques can be applied for continuous analysis of the validity of a calibration curve over an extended period of time, when monitoring a system's operation, and to detect when the calibration curve needs to be updated, as well as to indicate areas of potential improvement in laboratories.

It is appropriate to use QC data under intermediate conditions for estimating measurement uncertainties. The Anderson–Darling technique, which is a top-down approach, is superior to the bottom-up approach, and can prove favourable in evaluating statistical uncertainties of measurement systems. The dynamic uncertainty contribution of an analytical measurement system leads to uncertainties in the fitting function; therefore, pooling together the effects of various variances to an ultimate extent can be achieved without the complicated computation encountered using the bottom-up approach.

If an AAS system cannot give statistically sound results, all measurements are in vain. This study is of important practical significance and the research results can be widely used in similar statistical analysis of controlled processing.

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