QUALITY CONTROL DURING ANALYSIS OF POLLUTANTS IN BEER USING STATISTICAL CONTROL OF SURROGATE STANDARD

Abstract: In the framework of good laboratory praxis the emphasis is placed on the quality of reproducible results. Methods of mathematic statistics are very useful for this reason. In the form of regulating diagrams they can help to quick identification of that results which are outside the required tolerances. There are a lot of various samples used for statistical regulation. One possibility how to control the efficiency of whole analytic process, from preparing to the final determination, is using of surrogate standard. 2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl were used as surrogate standards for the determination of PCB in various types of water. These compounds were examined during relatively complicate determination of PCB in beer. The concentration was determined by Shewhart's diagrams for individual values and sliding span according to standard ČSN ISO 8258. This example of PCB determination in beer indicates the possibility of using surrogate standards as a powerful tool for determination of quality results.

Keywords: pollutants, PCB, surrogate standard, Shewhart's diagrams, beer

Good laboratory practice places great emphasis on systems assuring quality control of produced results [1]. Not always analytical methods work in the way to provide acceptable measurement results. The objective of quality assurance is to keep the produced results within constant and defined limits of which we assume to be correct. Ideally, the analysis results of check samples move around to the average value. But the size of this oscillation is time-dependent. The accuracy of measurement results might then be out of required tolerance and can get worse as a consequence of uncontrolled variation sources. Analysts need to have a tool available which would warn them soon enough that the analytical system moves out of the required zone of stability. Such a time warning can be provided by statistical quality control [2].

Walter A. Shewhart is considered the father of modern statistical control, who published a comprehensive work in 1931, dealing with this subject. The first control charts used for process quality control were elaborated already in 1924, when he was employed at Bell's laboratories of Western Electric Company [3].

Statistical quality control gained its ground mainly in production processes as a significant tool for production control. Nevertheless, a measurement process as well, including chemical analysis, is a certain kind of production, too. In this case, it is data production, on which similar quality requirements like on the product are posed. Very useful tools in statistical quality control are the control charts, which allow a fast visual check of the status of the system being controlled.
In general terms, control charts are used for the analysis of repeated processes, thus analytical measurements in our case. In principle, they are represented by continuous charts with statistically defined control elements.

The central line is the first control element, which is considered to be the mean value of measurement results that are uniformly distributed around it. It would be optimal if this line (its numerical representation) was identical with the real content of the check material. In reality, this never happens and therefore, the value of the central line is derived from the mean value of a series of measurement by a stabilised system, about which it can be stated that it is in the status of statistical control. To determine this value, at least 20 repeated measurements in a sufficiently long period of time are recommended to be carried out, which is necessary to involve the time dependence of the system.

Control limits are the second element and are defined as \( \pm k \)-multiple of the mean-root-square error of determination. Since the deviations can be both positive and negative, also these limits are called upper and lower limits \([2, 4]\). Shewhart’s diagrams are the most frequently used type of control diagrams in chemical analytical laboratories for the control of the accuracy of the analytical method. The controlled parameter is the value of the concentration of the corresponding analyte, which is plotted against the time axis representing individual measurements. The diagram produced from individual results is called the diagram for individual values. A second alternative is the measurement of the check sample repeatedly at each series, most frequently in a pair. In this case, average values of repetition are plotted in the diagram. The diagram produced from average values represents a more sophisticated but more exacting and more expensive alternative. Its advantage is that the influence of the random error is reduced by using the averages of repeated measurements of the same check sample and the probability of the detection of systematic errors, which fundamentally determine the accuracy of the analytical procedure, increases.

These diagrams are frequently used in connection with the diagrams for moving ranges, which are designated for the control of the presence of random errors and are not influenced by a possible systematic error. The moving range is the absolute value of the difference of a pair of measurement following each other in a measurement series, ie the difference between the first and second measurement, then between the second and third measurement, etc. \([2, 4]\).

For statistical control, various check samples are used for the measurement, such as a blank test of the method used (checks, whether the laboratory environment, chemicals or equipment do not contain contaminated substances or other interference compounds), a fortified matrix (a real sample with known addition of the analyte being determined is analysed in the same way as the real sample, it is used to discover systematic errors), a laboratory duplicate (two parts of the same sample are analysed separately in the same way, it is used for monitoring of the accuracy of the laboratory measurement, it discloses possible random errors) \([5, 6]\).

Even if these check samples are analysed with a pre-defined frequency, they can not involve a random error which could occur when preparing a certain sample. This problem can be resolved by using the surrogate standard.

The surrogate standard is an additional check analyte. It is an organic compound, the presence of which in the sample is in practical terms unlikely and which has similar physical and chemical properties as the analytes being determined. The known quantity of
this substance is added to all blank tests, calibration and check standards, to each sample (including duplicates and reference samples), always before the analytical procedure is carried out. The samples are then analysed ordinarily. The purpose of this additional analyte is to monitor the effectiveness of the analytical method absolutely for each sample [7, 8].

The determination of PCB in beer is quite complicated and consists of several steps - separation, purification, concentration increase [9]. These operations are critical points of the entire method and can be a source of errors. The control of the whole analytical procedure by means of a suitable surrogate standard is thus an important part in the assurance of the quality of produced results. For PCB determination in various water types, the following two substances were proven to be the best to be used as the surrogate standard: 2,4,5,6-tetrachloro-\(m\)-xylene and decachlorobiphenyl [10, 11].

The aim of the work was to test the possibility of using these two substances for statistical control using Shewhart’s control diagrams as the tools of quality control for the determination of PCB in beer.

**Experimental**

**Chemicals and standards**

- \(n\)-hexane SupraSolv, diethyl ether p.a., Extrelut - Merck, Germany;
- Florisil PR 60 - 100 mesh, anhydrous natrium sulphate - Fluka, Switzerland;
- Ultra-pure water - Milli-RO 5 plus - Millipore, USA;
- Nitrogen of grade 4.6 and nitrogen of grade ECD - MGO, Czech Republic;
- PCB - Mix 3 containing PCB congeners No. 28, 52, 101, 118, 138, 153, 180. The mixture was in isooctane and acetonitrile solutions, each congener at the concentration of 10 ng/mm\(^3\) - Dr. Ehrenstorfer, Germany;
- 8080 Surrogate Spike Mix containing 2,4,5,6-tetrachloro-\(m\)-xylene and decachlorobiphenyl, each substance in acetone solution at the concentration of 1 ng/mm\(^3\) - Supelco, USA.

**GC conditions**

- Gas chromatograph: Chrompack CP 9001;
- Column: DB-5, length 30 m, diameter 0.32 mm, film thickness 0.25 \(\mu\)m;
- Carrier gas flow rate (nitrogen): 1.8 cm\(^3\)/min;
- Detector: ECD;
- Detector temperature: 310°C;
- Injector temperature: 260°C;
- Injection: splitless for 36 s, then split ratio 1:20;
- Temperature program: 70°C (2 min), 25°C/min to 200°C (0 min), 2°C/min to 250°C (0 min), 50°C/min to 290°C (10 min)
- Injection: 1 mm\(^3\)

**Sample preparation**

20 mm\(^3\) of the surrogate standards (2,4,5,6-tetrachloro-\(m\)-xylene and decachlorobiphenyl, each at the concentration of 1 ng/mm\(^3\) in acetone) are added into an exactly measured quantity of about 1 dm\(^3\) of a thoroughly defoamed beer sample. Then the sample is extracted by 20 cm\(^3\) of hexane for 15 minutes on a laboratory shaker with the
swing amplitude of 40 mm and a frequency of 70 to 80 swings per a minute. For separating
the extract emulsion from the analyse beer, Hrivňák’s adapter is used. The destruction of
the emulsion is made by its sucking through the column filled with 6 g of Extrelut sorbent
being previously activated by application of 9 cm³ of ultra-pure water. The flow rate of the
extract through the column with Extrelut is accelerated by connecting a water pump.

In the following step, it is necessary to purify the received hexane eluate in the column
with approximately 3 g of Florisil sorbent with a layer of about 0.5 g of anhydrous natrium
sulphate above it. Just before the use, the column is flushed with about 5 cm³ of hexane.
The hexane eluate received after having gone through the column with Extrelut sorbent is
thickened at laboratory temperature by blowing-off under nitrogen atmosphere to a volume
of about 1 cm³ and then it is applied in the column prepared together with Florisil sorbent.
Elution is carried out by 25 cm³ of a 6% solution of diethyl ether in hexane. The
concentration of the purified extract is first increased in Kuderna-Danish apparatus and
finally under a gentle stream of nitrogen to a final volume of 200 mm³. 1 mm³ of such
purified extract is then used for the analysis by the gas chromatography.

Results and discussion

The concentration of both surrogate standards was measured in 30 different beer
samples (8 pale draft beer samples, 13 pale lager samples, 3 dark draft beer samples, 4 dark
lagers and 2 non-alcoholic beer samples). From these results, the values for the central line
and the control limits for Shewhart’s control diagrams for individual values and the moving
range were calculated according to the following relations:

Diagram for individual values X:
Central line = $X$
Upper control limit = $X + 3/1.128 \times R$
Lower control limit = $X - 3/1.128 \times R$

Diagram for moving range R:
Central line = $R$
Upper control limit = $3.267 \times R$, lower control limit = 0,
where $X$ is the average concentration of the surrogate standard, $R$ is the average moving
range [3].

The concentrations of the surrogate standards from the samples analysed for the
purpose of routine checking were gradually plotted in such prepared diagrams. The control
diagrams for individual values and the moving range of both surrogate standards are shown
in Figures 1 and 2. From the course of these diagrams, an important fact can be observed -
the system is stable and it is in the state of statistical control. The positions of the measured
points at their time course meet the criteria used for the interpretation of this type of control
diagrams: none of the points lies out of the control limits and, eight consecutive points do
not lie on the same side of the central line [2].

Conclusion

2,4,5,6-tetrachloro-$m$-xylene and decachlorobiphenyl were successfully used as
surrogate standards for the determination of PCB in beer. By means of the statistical control
of the concentration value of these substances in the form of Shewhart’s control diagrams,
it is possible to control the maintenance of the measurement process in a statistically
managed status and detect as well as eliminate systematic errors and, as a result of this, the quality of produced results can be systematically assured.

Fig. 1. Shewhart’s control diagrams for individual values of concentration and moving span of 2,4,5,6-tetrachloro-

*ortho*-xylene
Fig. 2. Shewhart’s control diagrams for individual values of concentration and moving range of decachlorobiphenyl

References

Quality control during analysis of pollutants in beer using statistical control of surrogate standard


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Słowa kluczowe: zanieczyszczenia, PCB, standard zastępczy, diagramy Shewharta, piwo