DETERMINATION OF PHENOLIC COMPOUNDS IN INDUSTRIAL WASTE

Marjana Simonič

Faculty of Chemistry and Chemical Engineering, University of Maribor, 2000 Maribor, Smetanova 17, Slovenia
e-mail: marjana.simonic@um.si

Abstract

The aim of this work was to validate the concentration of phenolic compounds in waste using an aminoantipyrine spectrophotometric method. The validation of the method was carried out with leachate from industrial waste. Leachates from various industrial wastes were treated by an extraction process in which soluble components were removed from the solids. Millipore water was used as a solvent. The concentration of phenolic compounds was determined in leachates from the following materials: filter dust from the abrasives industry and filter dust from the aluminium industry. The validation included the determination of the measuring range, the detection limit, the limit of quantification, the linearity, the precision of the measurements, the accuracy and the influence of interferences. The results confirmed the precision and accuracy of the method. The method is suitable for determining the phenolic compounds content in industrial waste from the metal industry.

Introduction

Phenol is classified as an organic aromatic compound, which is not harmful to health in minimal concentrations of up to 0.1 mg/kg, but can become very harmful with prolonged exposure to the body. The European Community (EC) has classified them as priority compounds [1]. Phenol is used in the production of synthetic fibers, in the production of phenolic resin, in chemicals that kill bacteria (slimicides), is used as a disinfectant, is also an antiseptic and is found in medicinal preparations (e.g. throat lozenges, mouthwash, etc.). It is biodegradable, reacts with OH - radicals and ozone. Its estimated half-life in the atmosphere is approximately 14 days.[2] Phenol is produced in large volume, mostly as an intermediate in the production of other chemicals. Phenol index is an indicator of phenolic contamination expressed as total content of phenolic compounds in water [3]. Various materials are used in the production of grinding wheels. These include corundum-based particles, organic binders (e.g. phenol-formaldehyde resins to hold abrasive grains together) and various other additives. The gas and dust products generated in the production of grinding wheels are led through a cleaning device with filters, where the filter dust is collected. This dust contains high levels of phenol. It is disposed off in hazardous waste landfills. Due to the discharge of effluent from wastewater treatment plants, the concentrations of phenol in surface water increases [4].

Foundry sand is a byproduct produced during the aluminum casting process. It is primarily composed of quartz sand and contains approximately 1 % binder, typically a mixture of polymerized phenolic resin and isocyanurate. Classified as non-hazardous, this material can be repurposed for various applications, such as the production of floor tiles.

The aim of this work was to partially validate the concentration of phenolic compounds in leachate from industrial waste. The following validation requirements, such as correlation coefficient (*R*), the accuracy, precision, the limit of detection (*LOD*) and the limit of quantification (LOQ) were evaluated.

Experimental

The implementation of the method includes preliminary leaching according to the SIST EN 12457- 4:2004 standard [5], sample distillation, liquid-liquid extraction and measurement on a spectrophotometer. The preparation of the test sample was carried out in accordance with the SIST EN 15002:2006 standard [6].

The validation of the analytical method includes the working and measuring range, determination and confirmation of the detection limit and the quantification limit, linearity, precision (repeatability and reproducibility), accuracy (calculation of average recoveries) and interference study. The measurement uncertainty of the leaching was estimated from the repeatability uncertainty (*RSD*) of all samples. Figure 1 shows the real sample.

Figure 1. Grinding wheel filter dust real sample

Phenol reference material (Phenol [CAS:108-95-2] 1000 mg/L in Water), was prepared by dissolving in freshly boiled and cooled millipore water, transfered to a 1000 mL volumetric flask. The solution was stable for 1 week.

UV-Visible Spectrophotometer Cary 50 Bio, Agilent, USA, Multi 3410 WTW pH meter and COND 3110 WTW conductometer were used.

Samples were crushed and sifted, then leaching was done with HNO_3 in laboratory. After filtration (0.45 µm filter) and distilation the solid-liquid extraction with chlorophorm followed. 500 mL of destilate was extracted with 25 mL of chloroform. Blank and control samples are extracted the same way. Always control sample was treated the same way. The absorbance was measured at 456 nm. The dillution factor must be calculated. After extraction dry weight was calculated (SS).

The laboratory should be able to determine, whether imprecision or bias is the reason for its inaccuracy. Interlaboratory tests are one of the most important external quality assurance tools to assure comparability with all the other laboratories. Another option is based on the recovery calculation according to equation 1. Recovery for standard solutions was calculated at multiple concentration levels of a given linear concentration range. We set the criterion that the method is accurate when the average recovery value is within the interaval from 90.0 % to 110.0 %.

$$recovery = x_m / x_t \cdot 100 \qquad (1)$$

x_m: is the result reported by the measurement.
x_t: is the theoretical value.

Results and discussion

The dry weight was determined by dividing the mass of dried sample (at 105 °C) and the mass of sample which was not dried. The results showed, that the SS value was 99.8 % and 99.6% in dust from Al production and from grinding wheels production, respectively.

LOD was determined to be 0.2 µg/L, based on the standard deviation of the blank signals (s_b) and the slope of the calibration curve (m) after dilution of the standard solutions ($3s_b/m$).LOQ was determined at 0.7 µg/L.

Accuracy

To check the accuracy, we prepared standard solutions with concentrations of 50.0 µg/L (V1), 100 µg/L (V2), 250 µg/L (V3), 500 µg/L (V4) and 800 µg/L (V5) in the same way. Measured concentrations and recoveries, calculated according to equation (1), are seen from Table 1.

Table 1.Measured values and recoveries

Sample	x_m (µg/L)	x_t (µg/L)	Recovery (%)
V1	46	50	92
V2	109	100	109
V3	237	250	95
V4	522	500	104
V5	850	800	106

It is seen from Table 1 that all results were determined within the confiedence interval 92 % – 109 %. Recovery meets the criterion and the method is accurate.

Linearity

The concentration of phenolic compounds was measured in a chloroform extract. Figure 2 represents the calibration curve.

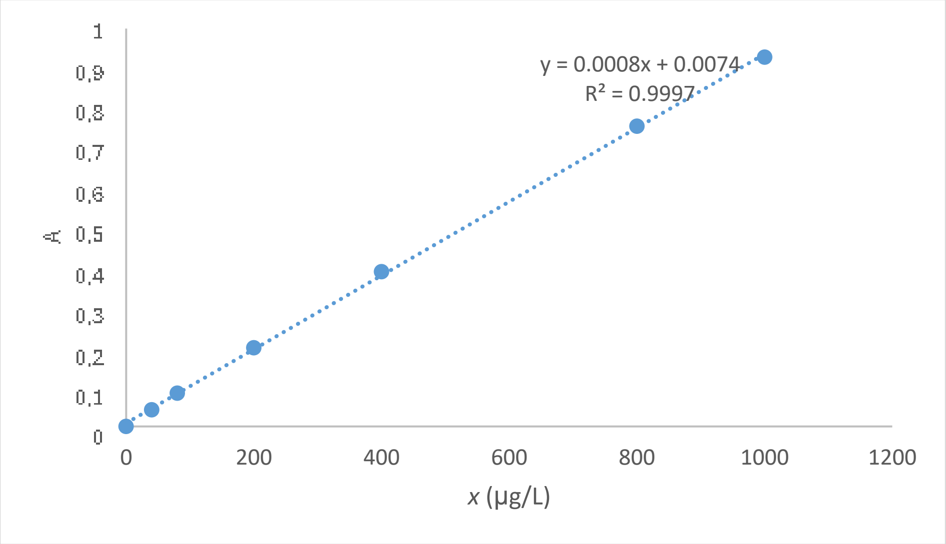

Figure 2. Calibration curve

The phenol concentration in the extract was first measured using a spectrophotometer, and then we calculated the initial leachate sample the 20times dilution was considered. The calibration curve with equation $A = 0.0008 \cdot x + 0.0074$ and high correlation coefficient $R^2=0.9997$ was determined. Quality coefficient was determined at 2.01.

Precision

The repeatability of the leaching was performed on four types of real leachate samples. From each sample, 6 leachate samples were prepared and analyzed under reproducible conditions (the same analyst, same analytical procedure, the same equipment, the same chemicals, etc.). From the obtained data, we calculated the standard deviation (*s*) and relative standard deviation (*RSD*). The *RSD* was obtained from 6 measurements of each sample. It was demonstrated that the *RSD* meets the standard requirements. The results of precision study are presented in Table 2.

Table 2. Data for precision determination

Sample number	$\bar{x}$ (µg/L) wheels	$\bar{x}$ (µg/L) Al dust
1	860	4.3
2	895	4.1
3	880	4.4
4	820	3.9
5	850	4.1
6	880	3.8
Average	864.2	4.1
s	26.9	0.2
RSD (%)	3.1	5.5

The results of reproducibility (under different conditions) showed low *RSD* value 3.1 % which is in accordance with requirements.

Interferences study

Interferences due to biological degradation, sulphur compound content or oil content as well as amine presence could influence the measurements. In such cases a preservative must be added. However, in our samples it was impossible.Therefore, the interference of amine addition was checked. Known volumes of trihydroxytriethylamine were added to 500 ml of a standard control solution of phenol with a concentration of c = 0.40 mg/L in chloroform. The procedure was carried out without distillation to avoid the removal of the interfering compound.

Table 3. Influence of trihydroxytriethylamine (amine) to the sample (*N*=sample number)

N	V_{amine} (mL)	$\bar{x}$ measured (mg/L)
1	0	0.41
2	0.5	0.41
3	1.0	0.40
4	4.0	0.42
5	8.0	0.42

Trihydroxytriethylamine was at least partially extracted into chloroform, which was also noticeable during the measurement, but the presence of this interference, as can be seen from the Table 3, did not have a significant effect on the determination of the concentration of phenolic compounds.The recovery was in range from 95 % to 105 % within the 95 % confidence interval.

Conclusion

The partly validation of the concentration of phenolic compounds was carried out on waste samples generated in the aluminum industry. The following validation requirements, such as correlation coefficient (*R*), quality coefficient (*QC*), the accuracy, the limit of detection (*LOD*) and the limit of quantification as well as interferences were evaluated. Linearity was checked with the quality coefficient *QC*, which was 2.01%, and the correlation coefficient R^2 was 0.999. The relative standard deviation (*RSD*) of repeatability was below 15 %. The accuracy of the analysis method was confirmed by the calculation of recovery. The concentration of phenolic compounds in waste sample generated in the aluminum industry was low, while it was quite higher in a waste sample from the grinding wheel industry.

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