COBALT QUANTITATIVE DETERMINATION IN THE ATMOSPHERIC EMISSIONS AND IMISSIONS BY SPECTROPHOTOMETRIC METHOD

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Abstract. Since 1993 the atmospheric emissions control from stationary sources became an obligation for the units/factories and for the institutions affiliated with the atmospheric pollution control. The Order No 462/1993 of the Waters, Forests and Environmental Protection Ministry makes limitations for over 150 organic or/and inorganic pollutants including cobalt and its compounds. STAS 12574/87 ‘Air of Protected Zones. Quality requirements’ do not establish limits for cobalt. In our country, even in UE, do not exist normalised chemical methods for cobalt determination in fluid gas and particulate or for air quality. As a member of the Technical Committee INCD ECOIND is involved in the activity of Romanian Standard (RS) elaboration in the field. This paper presents the results obtained for the cobalt-nitroso R spectrophotometric method. This method will be applied together with the flame AAS in a proficiency testing according to ISO IEC Guide 43-1, in 2002 and 2003.

Keywords: stationary sources, emission, cobalt, nitroso R, spectrophotometry, proficiency testing.

AIMS AND BACKGROUND

All activities for environmental control/monitoring require:  
- Existence of methods for quantitative analyses of water, soil, air quality and fluid/exit – EG – gases with high level of reproducibility and repeatability;  
- Promotion of modern, exact, reproducible and repeatable control method elaborating projects in concordance with the European legislation specific in the field of standardisation and conformity assessment;  
- Test laboratories accreditation in accordance with ISO/CEI 17025:2000.

The particulate matter/dust from the exit gases from the stationary sources of industrial plants or incinerators can contain different metals like Cd, Pb, Ni, Mn, Cr, Co.

The Emission Limit Value (ELV) for cobalt and its compounds is 0.5 mg/m³ fluid gas.

* For correspondence.
EXPERIMENTAL

Taking into account the equipment existing in most of the Romanian analytic laboratories, the R5 project elaborated by INCD ECOIND for cobalt emission/imissions measurements to the stationary sources or for air quality, after laborious experiments, included two methods:

- Nitroso R VIS spectrophotometric method;
- AAS method.

We experimented the Nitroso R-vis. spectrophotometric method. Sampling - the first and most important step - was carried out:
- by air aspiration and Sartorius cellulose acetate filter retention using a specific flow air;
- by air aspiration and Sartorius glass filter retention using a specific flow air to assure isokinetic sampling.

Dissolution was made in specific acid mixture taking into account the composition of the dust: $H_2SO_4/HNO_3; HCl/HNO_3; HCl/HNO_3/HClO_4$.

Standard solution of 10 $\mu$g Co/ml solution, used for calibration curve, was prepared from:

- metallic cobalt (99.99% purity);
- $CoCl_2\cdot6H_2O$ (min. 99.90% purity).

Calibration curve (Table 1):
- 0 to 10 ml standard solution of 10 $\mu$g Co / ml in 50 ml volumetric flasks;
- pH establishment using sodium acetate;
- nitroso R complex formation after boiling in water bath for 10 min;
- stabilisation of nitroso R complex formed by using nitric acid solution;
- the equipment used for the analysis was CINTRA 5 spectrophotometer, photometric readings at 520 nm.

Table 1. Co / nitroso R calibration curve records

<table>
<thead>
<tr>
<th>$\mu$g Co in 50 ml final solution</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>mean</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>0.0508</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0508</td>
</tr>
<tr>
<td>20</td>
<td>0.0958</td>
<td>0.0965</td>
<td>0.1097</td>
<td>0.1020</td>
<td>0.0988</td>
</tr>
<tr>
<td>30</td>
<td>0.1430</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1430</td>
</tr>
<tr>
<td>40</td>
<td>0.1880</td>
<td>0.1881</td>
<td>0.1820</td>
<td>0.1837</td>
<td>0.1855</td>
</tr>
<tr>
<td>50</td>
<td>0.2328</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2328</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>0.2757</td>
<td>0.2763</td>
<td>0.2830</td>
<td>0.2783</td>
</tr>
<tr>
<td>80</td>
<td>0.3710</td>
<td>0.3736</td>
<td>0.3734</td>
<td>0.3783</td>
<td>0.3741</td>
</tr>
<tr>
<td>100</td>
<td>0.4617</td>
<td>0.4621</td>
<td>0.4664</td>
<td>0.4664</td>
<td>0.4642</td>
</tr>
</tbody>
</table>

This method was verified in an interlaboratory proficiency testing scheme in 2002.
Table 2. Interlaboratory results

<table>
<thead>
<tr>
<th>SRS</th>
<th>Laboratory</th>
<th>1</th>
<th>2</th>
<th>3*</th>
<th>4**</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9**</th>
<th>X_p</th>
<th>Med.</th>
<th>S</th>
<th>C_v</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRS P7</td>
<td></td>
<td>5.71</td>
<td>6.00</td>
<td>5.69</td>
<td>5.45</td>
<td>5.84</td>
<td>5.61</td>
<td>5.74</td>
<td>5.83</td>
<td>5.78</td>
<td>5.74</td>
<td>5.74</td>
<td>0.15</td>
<td>2.70</td>
</tr>
<tr>
<td>SRS P8</td>
<td></td>
<td>17.08</td>
<td>17.60</td>
<td>17.32</td>
<td>17.67</td>
<td>17.36</td>
<td>17.18</td>
<td>17.22</td>
<td>17.41</td>
<td>17.27</td>
<td>17.35</td>
<td>17.32</td>
<td>0.19</td>
<td>1.11</td>
</tr>
<tr>
<td>Z1</td>
<td></td>
<td>0.19</td>
<td>1.68</td>
<td>0.32</td>
<td>1.87</td>
<td>0.65</td>
<td>0.84</td>
<td>0.00</td>
<td>0.58</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z8</td>
<td></td>
<td>1.41</td>
<td>1.30</td>
<td>0.66</td>
<td>1.67</td>
<td>0.05</td>
<td>0.89</td>
<td>0.68</td>
<td>0.31</td>
<td>0.42</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Z6 score</td>
<td></td>
<td>0.80</td>
<td>1.49</td>
<td>0.49</td>
<td>1.77</td>
<td>0.35</td>
<td>0.87</td>
<td>0.34</td>
<td>0.45</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* ICP AES analysis; ** AAS analysis.
Using high purity reagents (Merck) and taking into account the range of the calibration curves for spectrophotometric determination of cobalt, two Synthetic Reference Solutions (SRS) were prepared. These SRS were distributed to the nine laboratories participating in the proficiency testing scheme.

The specialised laboratories participating in the project were the following: S. C. CAST S.A., S.C. LACECA S.A., I.C.I.M., S.C. REPUBLICA S.A., INCIDPM, Environmental Protection agency from Ploiesti, SC ROMPETROL PETROMIDIA and INC D ECOIND.

From confidentiality reason, the laboratories were identified by numbers ranging from 1 to 9 (Table 2).

For statistical interpretation of the interlaboratory results were calculated:
- the mean value of the interlaboratory results \( X_p \) / considered as reference consensus value;
- the standard deviation of the interlaboratory results \( S \);
- the relative deviation of the interlaboratory results \( C_r \);
- the individual Z score \( Z_i \) and total Z score \( Z_t \):

\[
Z_i = \frac{x_i - X_p}{S}, \quad Z_t = \frac{Z_i + Z_j}{2}.
\]

CONCLUSIONS

- Good repeatability and reproducibility of the method.
  - All laboratories obtained \( Z_i \) score < 2 which represents very good performance.
  - The results will be used for method validation in a CALIST National R&D project.

REFERENCES

6. ISO 5725 Accuracy (Trueness and Precision) of Measurement Methods and Results. Part 1 to 6.

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