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# SAMPLING METHOD OF $Cr^{6+}$ FROM STATIONARY SOURCE EMISSIONS

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## *Introduction*

The toxicity of $Cr^{6+}$ compounds has led to a number of studies aimed at identifying and quantifying them in the environment. The developed methods are based primarily on the chemistry of chromium but also on the specificity of the matrix from which it is determined with reference to the level of concentration, pH, degree of hydrolysis, redox potential, and level of complexation and/or sorption. Sampling is an important part of $Cr^{6+}$ determinations of residual gaseous effluents from stationary sources. Thus, $Cr^{6+}$ must be sampled and kept in the same state until analysis. The development of the $Cr^{6+}$ sampling method from the emissions of stationary sources involved the establishment of optimal sampling conditions, sample preparation and analytical quantification but also the validation of the method by determining the performance parameters and verifying the adequacy for the purpose. The method was applied in real conditions to a glass factory.

## *Materials and methods*

A special influence on the stability of chromium compounds is the pH of the matrix, which, in the absence of specific complexants, determines the form in which chromium species were founded in solution. So, at a pH value lower than 1, $Cr^{6+}$ was found in aqueous solution in the form of $H_2CrO_4$. In the range 1 to 6.5 of pH values, as a result of deprotonation, in the solution were founded a mixture of $Cr_2O_7^{2-}$ and $HCr_2O_7^-$, and finally, at a pH value higher than 6.5, $Cr^{6+}$ was in the form of $CrO_4^{2-}$.

In acidic environment, $Cr^{6+}$ has a strong oxidizing character, in such case in the presence of organic substances and other compounds with reducing character ($Fe^{2+}$ and $S^{2-}$) are reduced to $Cr^3$. Hence the need to maintain a basic pH throughout the sampling and preparation of samples for $Cr^{6+}$ stability, this being a criterion for verifying the correctness of sampling; this pH range also ensures the precipitation of $Cr^{3+}$ in the form of $Cr(OH)_3$.

To estimate $Cr^{6+}$ from stationary source emissions, two analytical methods have been developed. First method using molecular absorption spectrometry (UV-VIS) was applied for emissions from galvanic coating processes (decorative chromium plating and hard chromium plating). The second one intended to determine the low concentrations of $Cr^{6+}$ resulting from the incineration of waste and the glass industry use atomic absorption spectrometry method with atomization in the graphite furnace (GTAAS) after complexation with 1,5-diphenylcarbazide and concentration by extraction in isoamyl alcohol. Extraction in isoamyl alcohol ensures separation of $Cr^{6+}$ from $Cr^{3+}$ and preconcentration of the sample.

***Results and conclusions***

The following equipment was used for sampling: TESTO 350 XL analyzer, Paul Gothe isokinetic sampler equipped with glass probe. An AA280 FS Atomic Absorption Spectrophotometer and CINTRA Molecular Absorption Spectrometer were used for sample analysis.

The isokinetic sampling is performed with a heated glass, quartz or teflon probe, in order to retain $Cr^{6+}$ in an absorbent solution (fig. 1). For low concentration of $Cr^{6+}$ is used 0.1M NaOH (GTAAS method), 0.5M NaOH for emissions with high concentrations of $Cr^{6+}$ (UV-VIS method), or if the gaseous effluent was highly acidic (high concentrations of $SO_2$, $NO_x$. HCl, HF, etc.).

Maintaining the pH value higher than 8.5 in the absorbent solutions from the absorbers (9) represents one of the conditions for validity of the sampling. Other conditions are also maintenance in limits of the isokinetic conditions and the analysis of the field control samples.

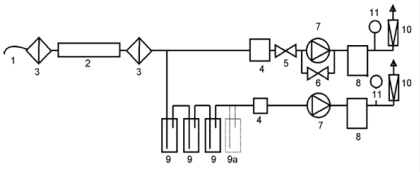


**Figure 1.** Schematic of an isokinetic system for filter air sampling and absorbent solutions

The results of the $Cr^{6+}$ isokinetic sampling that was performed at the dispersion chimney of a glass melting furnace were presented in tables 1 and 2.

**Table 1.** Physical parameters of the source

| Source | Diameter (m) | Area ($m^2$) | Velocity (m/s) | Height (m) | Temparature ($^oC$) | Flow rate | |
|---|---|---|---|---|---|---|---|
| | | | | | | mc/s | Nmc/s |
| Melting Furance | 3.0 | 7.07 | 7.1 | 85 | 218 | 50.0 | 27.85 |

**Table 2.** $Cr^{6+}$ concentration in stationary source emissions

| Source | Pollutant | Unit | Concentration |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| Melting Furance | *$Cr^{6+}$ | mg/Nmc cu 8% $O_2$ | 0.002 |
| | **$Cr^{6+}$ | mg/Nmc cu 8% $O_2$ | < 0.04 |

In conclusion, after the validation of the method by determining the performance parameters and verifying the adequacy for the purpose, this method can be applied in real conditions to pollutant dispersion chimneys.

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