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Speciation analysis of mercury in water effluents from the petroleum industry using cold vapor atomic fluorescence spectrophotometry

Sarzamin Khan[1] (PQ), Rodrigo A. Gonçalves[1] (PG), Maria Luiza B. Tristão[2] (PQ), Roberta M. T. de Mattos[2] (PQ), Ricardo Q. Aucelio[1] (PQ)

[1]Pontifical Catholic University of Rio de Janeiro, Department of Chemistry, [2)] CENPES-Petrobras; sarzamin81@gmail.com.

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Introduction

Mercury is one of the hazardous environmental pollutants and the extent of toxicity is closely related to its chemical form, which mainly occurs as elemental mercury (Hg^0) and inorganic mercury (Hg^{2+}). However, metalorganic forms, most predominantly methylmercury (CH_3Hg^+)[1] also exist. Depending on the source, mercury can be present in petroleum thus extraction and refining activities may contaminate the water associated to these processes (produced water) with mercury species that may pollute other water bodies if released to the environment. It is well established now that any type of mercury released to the environment can undergo biogeochemical processes resulting in the extremely toxic CH_3Hg^+. In Brazil, the maximum concentration for total mercury in aqueous effluents is 0.01 mg L^{-1}, but the assessment of lower values are important since environmental agencies always revise such limits as legislation tend to become more rigorous. Atomic fluorescence spectrometry (AFS) is very sensitive for mercury and when combination with GC, enables speciation analysis for many species of mercury. However, sample pretreatment and analyte derivatization are required.

Results and Discussion

Speciation analysis of mercury was performed using a GC-AFS analytical system (MERX, Brook Rands Co., USA). Methylmercury and inorganic mercury (Hg^{2+}) were converted into volatile species (methylethyl mercury and diethyl mercury) by aqueous phase ethylation with sodium tetraethylborate. The sample containing the mercury was transferred to a bubbler where a flow of argon gas (99.999%) all mercury species for the trap system to be adsorbed, dried and then desorbed to be further separated by a GC column. After separation, pyrolysis converts all mercury species into Hg^0 to be detected using a cold vapor atomic fluorescence detector. Pure standards solutions were used for calibration.

Under the established conditions (398 mL/min of argon purge flow; 34 mL/ min of argon carrier flow; column temperature of 35°C) a typical chromatogram is shown (Figure 1). Different species of mercury are fully separated with characteristic retention times. Since all of the different mercury species are detected as Hg^0, the analytical response for all of them are the same. The linear dynamic range covered the concentration range between 0.5 to 250 pg (as Hg^0) with a correlation coefficient of 0.9995. The limit of detection was 0.1 pg (reported as the lower concentration of Hg^0 detected using the baseline signal + 3s, where s is the standard deviation of the signal).

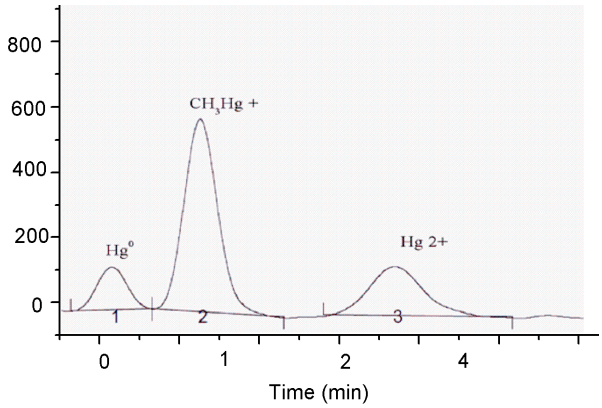

Figure1. Chromatogram for determination of different mercury species.

Conclusion

GC-AFS is a simple and reliable analytical approach for the determination of different mercury species. The volatilization of mercury by derivatization remove the analyte form the complex oiled sample, minimizing interferences imposed by organic matter and the characteristic salinity. Fluorescence detection enabled a very low limit of detection for all of the mercury species (detected as reduced mercury).

Ackonwledgement

CAPES, CNPQ, FAPERJ

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