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Application Note 079

DETERMINATION OF MERCURY IN NAPHTHA USING THE MILLENNIUM MERLIN

Introduction

Mercury is found naturally over a wide concentration range in petrochemical feedstock such as crude oil and natural gas condensate. During the refining process the mercury has a tendency to pre-concentrate in the lighter fractions. The distribution of Hg in the various hydrocarbon fractions will largely depend on the speciation of Hg within the feedstock. In most cases an appreciable amount of mercury will be transferred to the naphtha fraction. The naphtha is a valuable feedstock for catalytic and thermal cracking to produce a wide range of immediate products and the presence of Hg can be detrimental to these processes. In particular even low levels of Hg are known to cause catalyst poisoning reducing the lifetime of the catalyst dramatically. Mercury may also cause corrosion of aluminium heat exchangers and rotors. Without adequate Hg removal procedures the presence of Hg may cause financially crippling plant shutdowns. As a result of these implications, naphtha with a Hg concentration below 1ppb can be sold at a high premium and is in high demand. The measurement of Mercury in naphtha is difficult especially below 1ppb. Naphtha produced from steam distillation may contain quantities of water above saturation and particulate material from pipeline corrosion products. These contaminants often contain high levels of Hg and if not analyzed low results may prevail. In reality, the fate of Hg associated with these fractions is unknown and it is quite possible that this Hg will settle in storage tanks and not be distributed to the final products. The wet chemical digestion method has been developed to maximise the sample volume and thus give a total Hg measurement including the Hg associated with the particulate and water contaminants. This application note describes this procedure in detail. All samples are analysed using CV-AFS using the PSA Millennium Merlin.

Sample Digestion

Naphtha samples collected before and after a mercury removal unit (M.R.U.) were shaken on an automatic shaker for 5 minutes then 50 g of sample was weighed into a clean 200ml amber bottle. This helped obtain a representative sample. To this 40 ml of Aqua Regia (Aristar grade, 3:1 Ratio HCl:HNO_3), was added and the samples were shaken for 30 minutes. Following this the samples were transferred into clean reflux flasks were they were refluxed for one and the half hours. The samples were then cooled and the lower aqueous layer was separated with separating funnel into a 100ml volumetric flask and made to 100 ml volume with deionised water. In addition the samples were spiked with a known amount of mercury and analysed the same way. The samples were then diluted taking a 5 ml aliquot of solution and diluting to 50 ml with deionised water.

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The samples were then analysed using the Millennium Merlin. The instrument used 2% m/v $SnCl_2$ in 10%v/v HCl as reductant and 3% v/v HCl, 1% v/v HNO_3 as regent blank. Calibration standards were 0-3 ng ml^{-1} Hg prepared in the reagent blank. Figure 1 shows a typical calibration curve for mercury, showing the excellent linearity. Figure 2 shows the method settings used.

Figure 1

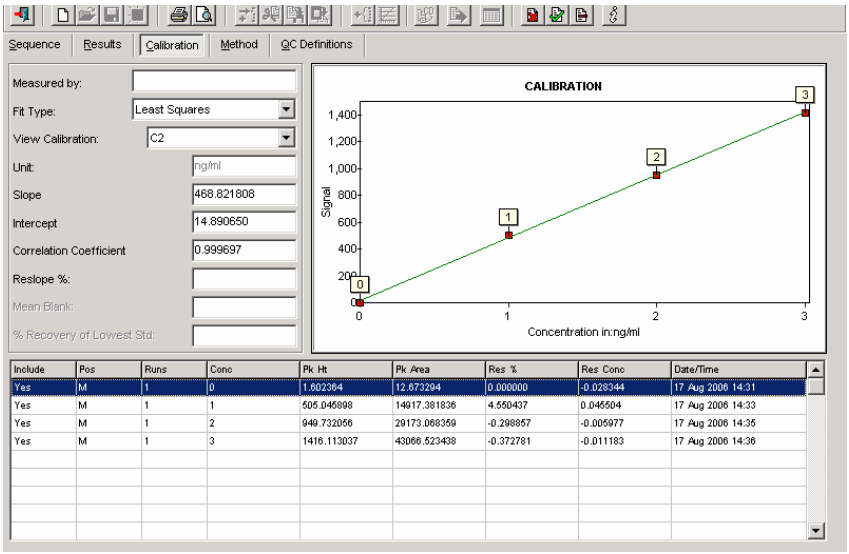
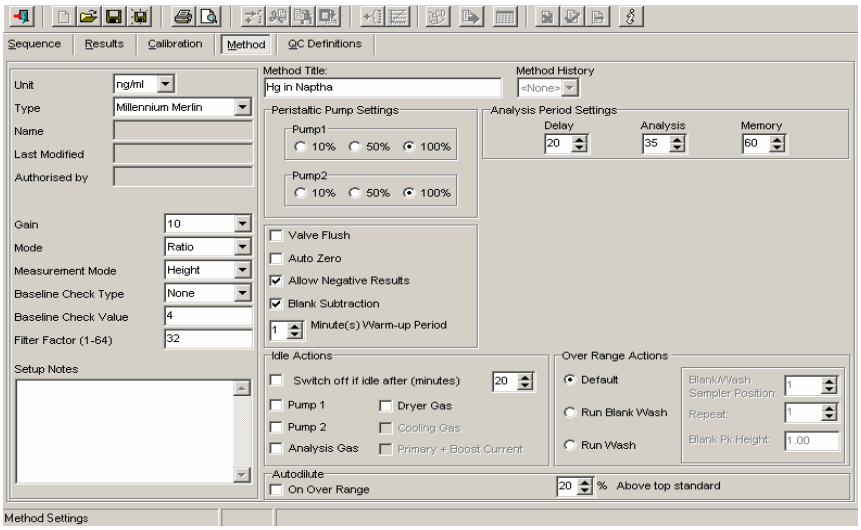


Figure 2



Results

The results obtained for the two samples are shown in table 1. The Method Limit of Detection (M.L.O.D.) under these conditions was found to be 0.047 ng g^{-1}. This could be improved by initially taking larger samples, for example, 200g instead of 50g.

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Table 1

Sample	Concentration found (ng g^{-1})	Expected Concentration (ng g^{-1})
Inlet	104.2 ± 1.0	-
Outlet	1.6 ± 0.7	-
CRM Conostan Hg	20.3 ± 0.3	20

Conclusions

Continuous flow vapour generation coupled to atomic fluorescence was used successfully to determine mercury in naphtha samples. The results show good accuracy and precision. Excellent spike recoveries were obtained validating the method procedure used and showing no matrix interferences present.

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