Online Arsenic Measurements in Refinery Wastewater using the PSA 10.256 Online Excalibur

Application Note APP189

Introduction

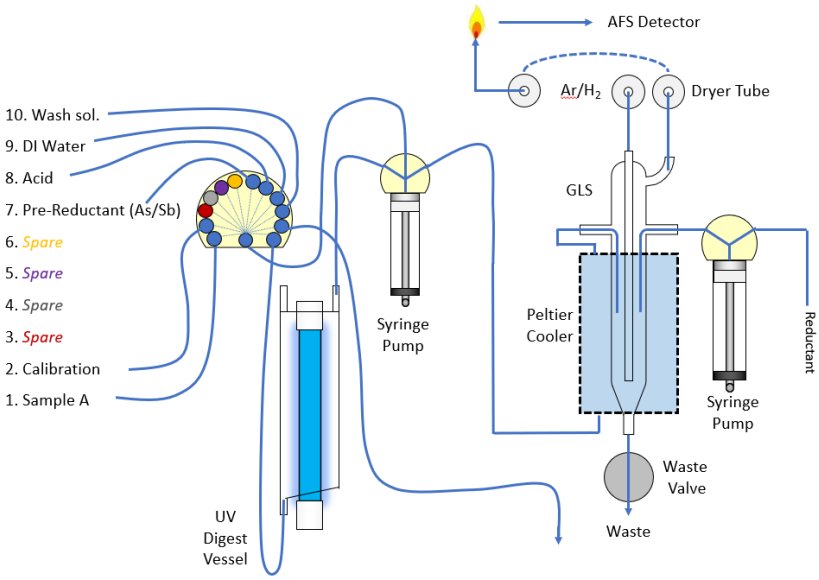
Oil and gas refineries are found across the globe, with aims to process a crude oil/natural gas and convert it to a profitable end products. Unfortunately, undesired by-products such as wastewater are also formed as part of the process. The wastewater must be discharged in accordance with locally set limits so to avoid fines and environmental damage.

In this application note, we demonstrate the performance of the new PSA 10.256 Online Excalibur. Two wastewater samples from different refineries were analysed to establish the levels of arsenic present. Samples were spiked with known concentrations of As(V) to ensure no matrix interference from the sample and demonstrate efficient conversion to As(III). Filtration was also carried out on some samples to determine if arsenic was associated with particulates.

The PSA 10.256 Online Excalibur

The 10.256 Online Excalibur has been designed for automated operation. It is equipped with an online digestion module and a syringe pump to introduce and inject reagents into the system. The analyser and a schematic of the chemistry section is shown in Figure 1. The Online Excalibur utilizes Hydride Generation - Atomic Fluorescence Spectrometry as a means of detection, offering unrivalled linear ranges and great sensitivity.

Figure 1 PSA 10.256 Online Excalibur with Operation Schematic



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Method

Wastewater samples from two refineries were analysed as grab samples. The sample from the USA contained some particulate material so it was run filtered and unfiltered to determine the effect of filtration on the sample. The sample was filtered using a Whatman Grade 41 ashless filter paper, which filters out particulates larger than 20 µm.

Each sample was digested online for 15 minutes. The digestion step used UV light along with a hydrochloric acid and potassium iodide pre-reductant to convert all arsenic species present to As(III). UV aids the photolysis of organo-arsenic compounds in the sample and the KI reduces As(V) to As(III). The digested sample was then moved via syringe pump to the Gas-Liquid Separator and reacted with a sodium borohydride reductant. This converts all As(III) to gaseous arsine, which was purged from the solution with hydrogen and argon carrier gases. The arsine was introduced to a flame in the detector, where it was atomised. Elemental arsenic was then excited using the boosted discharge hollow cathode lamp and the emitted wavelengths were detected using a solar bind PMT. Table 1 shows the reagent and gases used for analysis. In total, 2.5ml of sample and 7ml of reagents are used for each analysis analysis: 5ml acid, 1ml KI and 1ml $NaBH_4$.

Table 1 Utilities used for the 10.256

Parameter	Condition
Acid	50% v/v Hydrochloric acid
Reductant	0.7% m/v Sodium Borohydride, 0.4% m/v Sodium Hydroxide, 0.3% m/v EDTA
Pre-reductant	25% m/v Potassium Iodide, 5% m/v L-ascorbic acid
Standards	Made in 1% v/v Hydrochloric acid solution using As(III) stock solution
Carrier Gas	Argon @ 3 Bar g, 99.99%+ purity
Dryer Gas	Instrument air @ 4 Bar g, clean dry and oil free
Fuel Gas	Hydrogen @ 0.7 Bar g, 99.99%+ purity

Calibration

The analyser was automatically calibrated. The system can calibrate up to 1ppm. For this application, the top calibration standard used was 100ppb. An example calibration can be found in Figure 2. This calibration used calibration points 0, 10, 25, 50, 100 ppb. Calibrations using one standard can be performed to reduce the number of standards needed for preparation.

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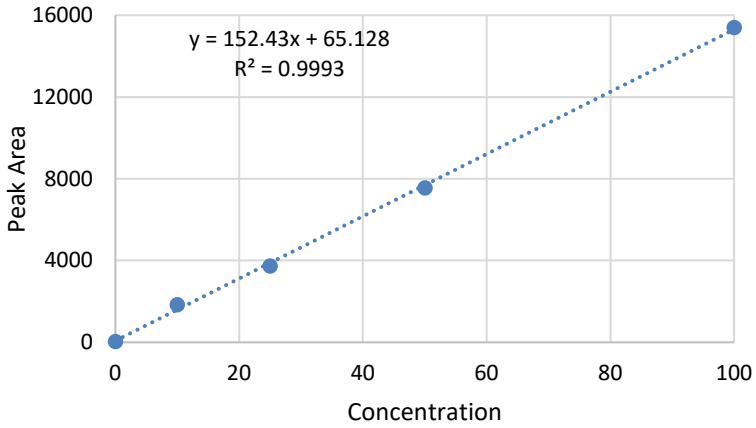
Figure 2 Typical 10.256 Online Excalibur Calibration



Results and Discussion

A summary of results can be seen in Table 2. Each wastewater sample was spiked with As(V) to demonstrate the efficient conversion of arsenic and ensure no sample matrix effect on the result. Recoveries for the spiked samples were between 96.5 to 99.4%, indicating no matrix effect for the analysis. The sample from the USA was run filtered and unfiltered. Results showed that filtration had no effect on the results indicating that arsenic was not associated with particulates in the sample.

Table 2 Summary of Results for Arsenic in Wastewater Samples

ID	Parameter	Concentration (ppb)	Recovery (%)
USA Refinery Wastewater	-	15.22 ± 0.49	-
	Filtered	15.49 ± 1.08	-
	Spiked with 15ppb As(V)	29.70 ± 0.93	96.5
Tunisia Refinery Wastewater	-	0.72 ± 0.25	-
	Spiked with 20ppb As(V)	20.61 ± 1.47	99.4

Conclusion

Many environmental agencies are becoming more stringent in the allowed effluent limits of arsenic and other elements in wastewater. In turn, refineries are now required to be able to analyse their wastewaters for arsenic at ppb levels. The PSA 10.256 Online Excalibur is able to accurately determine the concentrations of total arsenic in wastewaters from refineries. The samples were spiked with As(V) and excellent recoveries were obtained. This proves no matrix effects from the wastewater and efficient conversion to As(III) for analysis. The filtered sample result was very similar to the unfiltered result, showing that arsenic in the samples were not associated with particulates.

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