

PS Analytical Review

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www.psanalytical.com



Purpose built facility near London













We can exploit a) Hg has a significant vapour phase b) the volatile metal- hydride formation

Why PSA Utilises Atomic Fluorescence

- Hydride forming elements and mercury all absorb and fluoresce in the UV region below 260nm where AES and AAS are relatively insensitive.
- High intensity excitation sources available.
- Low spectral interference-analyte separated from matrix by the hydride/vapour generation process.
- High selectivity-only the analyte corresponding to the excitation source will fluoresce.
- Excellent sensitivity and linearity.



Advantages of Atomic Fluorescence Spectrometry (AFS)

- Sensitivity attainable is controlled by the intensity of the light source
- Equipment can be less complex than that needed for AAS or AES
- High sensitivity attainable into the far UV where AAS and AES are insensitive
- Good linearity
- Low spectral interference
- High selectivity
- Analytical line summation

Excalibur Fluorescence Detector for As, Se, Sb, Te and Bi



Hydride Fluorescence Detector





Core Products Environmental



Millennium Merlin - CVAFS and 1631-Hg

- Lab analyser based on Cold Vapour AFS
- EPA 1631 Method uses gold amalgamation
- Chemical digestion with acidic oxidants
- Stannous chloride reduction of $Hg^{2\scriptscriptstyle +}$ to $Hg^{\scriptscriptstyle 0}$

Hg(II) + Sn(II) $Hg^{\circ} + Sn(IV)$

- Automated with 2 min cycle times and optional UV automated digestion
- Detection Limits less than 1 part per trillion. Linearity 5 orders of magnitude.
- No quartz atom cell to avoid carryover between samples
- Suitable for all types of wastewater and plant samples (coal, coke, ash, leachates, gypsum, sorbent traps, impinger solutions etc)





Millennium Excalibur Hydride Generation AFS - As, Se, Sb

- Laboratory Analyser for As, Se, Sb, Te and Bi Single Element detector defined by lamp.
- Samples require preparation prior to measurement, digestion and conversion to optimal oxidation state
- Automated NaBH4/Acid chemistry to produce gaseous hydrides and hydrogen diffusion flame.

$NaBH_4 + HCl + 3H_2O = 8H + H_3BO_3 + NaCl = MH_x + H_2$

- Part per trillion detection limits. Linearity to 10ppm. 1 min cycle time. Optional UV autodigestion and species conversion.
- Lower MDL than ICPMS as less dilution required
- Suitable for all types of wastewater and plant samples (coal, coke, ash, leachates, gypsum, sorbent traps, impinger solutions etc)









Speciation/Fractionation Studies



Hg CEM Stack Gas Typical Configurations



PSA





10.225/10.255 Liquid Online Hg, As & Se







Core Products Petrochemicals









Sir Galahad II (10.525)



For the determination of mercury in a wide range of gaseous media, including;

- ambient air,
- natural gas
- stack gases.

The Sir Galahad is based on amalgamation with atomic fluorescence spectrometry which is inherently more sensitivity than atomic absorption and offers advantages in terms of linearity, accuracy and precision.

ASTM D6350-98(2003) Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy

This test method covers the determination of total mercury in natural gas streams down to $0.001 \,\mu\text{g/m}^3$. It includes procedures to both obtaining a representative sample and the atomic fluorescence detection of the analyte. This procedure can be applied for both organic and inorganic mercury compounds.



Hg in Process Gases - Sampling and Analysis

At line gas sampling up to 3000 psi





- Sample is swept over this trap in gaseous form
- Traps all forms of Hg
- Can trap in excess of 82mg of Hg
- · Can be used at elevated temps
- Low cost and Reusable

PSA SIR GALAHAD

Analysis on the bench Sir Galahad II



Core Area - Bespoke systems



PS









Introduction

- PSA's experience providing bespoke analyser/test systems
- Examples of some laboratory test systems we have done.
- Discussion of what is possible.

Designing and providing an analyser system that meets the client's expectations and requirements



Gas Test Bed System 0000

- Designed to fit in client's walk in fumehood
- High concentration mercury feed
- 14 sample points (4 with ۲ dilution)
- Two bed trains with flow control/pumps etc

Gas Test Bed System Schematic

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PSA





Hg in Liquid Hydrocarbons





Hg in Aqueous Systems







As, Se and Sb in Waste Water Streams





As, Se and Sb in Waste Water Streams



PSA Online Software

- Proven platform for online automation
- Configurable to provide what the customer needs
- Capable of upgrade as and when required



PSA OnLine Process Control Software



- Full instrument control
- Highly configurable
- Simple user interface
- Alarm and result outputs by digital and analogue methods

PSA OnLine Primary User Interface



PSA OnLine Instrument Sequence Tab



PSA OnLine Instrument Status Tab



PSA OnLine Calibration Tab



PC



PSA OnLine Other

- Results Tables/logs
- Events display/log
- Maintenance Scheduling
- Report Generation:



Menu Structure:





PSA Online Systems

- Review of some typical configurations
- Some Typical data



Online Mercury Analyser for Hydrocarbon Gases





Online Determination of Mercury in LNG



Hg CEM Stack Gas Typical Configurations



PSA





A Power station in Kentucky Typical long term data - Wet scrubber site



• Stack Sample • Hovocal * dry Zero-level (0.00) • dry high level Hg0 (10.07) • stack sample cont

Parallel TGM in air from Sir Galahads Online 2 month period - Sweden Coastal Site





Data from Crematorium in UK







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PS



Online Hg in Liquid Hydrocarbons



Online Hg in Naphtha Results from MRU with Zero and 10ppbw Conostan Span Checks





10.225/10.255 Liquid Online Hg, As & Se





Schematic Diagram of Online Systems



T-Hg in Synthetic FGD Wastewater



LOD based on 10 FIA measurements with 100 microliter injection

LOD (3σ), ppt 6.6

Online Selenium



Two months operation with daily calibrations operating with same peristaltic pump tubing, reagent top up every 2 weeks.





Chemistry - Online As analysis





Schematic for Online System



Wastewater Online Arsenic Data





Precision and Bias Data for standards

Description	<u>Mean ± SD ng/ml</u>	<u>RSD%</u>	<u>%Recovery</u>
<u>0 ppb As (V)</u>	<u>0.66 ± 0.71</u>	<u>107%</u>	<u>n/a</u>
<u>50 ppb As (V)</u>	<u>50.21 ± 1.09</u>	<u>2.2%</u>	<u>100.4%</u>
<u>100 ppb As (V)</u>	<u>101.29 ± 0.40</u>	<u>0.4%</u>	<u>101.3%</u>
<u>200 ppb As (V)</u>	<u>204.34 ± 2.56</u>	<u>1.3%</u>	<u>102.2%</u>
<u>300 ppb As (V)</u>	<u>306.98 ± 8.06</u>	<u>2.6%</u>	<u>102.3%</u>
<u>50 ppb As (III)</u>	<u>47.69 ± 0.62</u>	<u>1.3%</u>	<u>95.3%</u>
<u>100 ppb As (III)</u>	<u>97.12 ± 0.94</u>	<u>1.0%</u>	<u>97.1%</u>
200 ppb As (III)	<u>191.53 ± 3.44</u>	<u>1.8%</u>	<u>95.7%</u>
<u>50 ppb As (V)</u>	<u>50.83 ± 0.31</u>	<u>0.6%</u>	<u>101.6%</u>
<u>100 ppb As (V)</u>	<u>100.92 ± 0.89</u>	<u>0.9%</u>	<u>100.9%</u>
<u>200 ppb As (V)</u>	<u>204.47 ± 3.07</u>	<u>1.5%</u>	<u>102.2%</u>
<u>300 ppb As (V)</u>	<u>311.88 ± 3.27</u>	<u>1.1%</u>	<u>103.9%</u>
<u>50 ppb As (III)</u>	<u>49.25 ± 0.32</u>	<u>0.7%</u>	<u>98.5%</u>
<u>100 ppb As (III)</u>	<u>98.75 ± 1.50</u>	<u>1.5%</u>	<u>98.8%</u>
200 ppb As (III)	<u>198.92 ± 3.88</u>	<u>1.9%</u>	<u>99.5%</u>



Comparison on Lab versus Online

Sample Description	Online Result ng/ml	Laboratory Result ng/ml
Wastewater Sample A	25.5 ± 0.8 (n=20)	23.6 ± 1.2 (n=4)
Wastewater Sample B	249.1 ± 4.8 (n=20)	242.4 ± 0.7 (n=4)

Sampling system with fast loop filter



All fluoropolymer (PTFE & PFA) wetted path

Filter sizes 1-25µm in Teflon. Larger sizes in other materials.

Self cleaning inertial filter, easily replaceable

Sample flow through filter is 0.8ml/min from a higher flow bypass circa few hundred ml/min or more

Filtration does not seem to influence results.

Internal bore of tubing on instrument is 0.6mm (i.e. 600 micron).

Pre-acidification options and dilution available.



Thank you for attention. Any Questions?

- Authorized Representative
- For Additional Information, Quotes, Power Points, & Specifications contact:
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