AMA254

Advanced Mercury Analyzer

The following article first appeared in the June, 2002 edition of World Coal and has been reprinted with permission.

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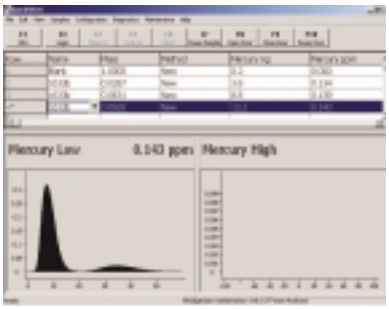
Advanced analysis

John Willming and Paul Pirozzola, LECO Corporation, US, investigate the solutions provided by the company's new mercury analyser in the wake of imminent, increased EPA regulations.

The AMA254 mercury analyser.

QuickSilver software's calibration screen is used with the AMA254 mercury analyser for the calibration of standards.



A capture of the QuickSilver operating screen used with LECO's mercury analyser. The peak is shown for the selected standard.

In December 2000, the United States Environmental Protection Agency (EPA) announced plans to eventually control power plant emissions of mercury, based on the results of an extensive study conducted by the agency. Currently, regulations have not been created, although the EPA will propose them by 2003 and issue final rules by 2004. The EPA study, which was a requirement under the Clean Air Act of the US Congress, was initiated in order to determine whether regulations were needed on power plant emissions and if those emissions posed significant hazards to human health. A 1998 EPA report to Congress concluded that mercury posed the greatest concern of all the toxic pollutants examined.

Causes

The EPA determined that approximately 60% of the total mercury deposited in the US came from air emission sources. This percentage is estimated to be even greater in specific geographic regions. Studies showed that the largest source of emitted human-made mercury pollution in the US came from coal-fired power plants, which were estimated to emit approximately 43 tpa. Coal-fired electric utilities generate mercury emissions that account for about half of the 60% total.

Mercury is emitted from additional sources other than power plants, including municipal waste combustors, medical waste incinerators and hazardous waste combustors. Other industrial sources of mercury emissions include cremation and cement making.

Effects

Mercury emitted into the air from power plants is often deposited into water bodies, where biological processes then transform it into methylmercury. This highly toxic compound can potentially build up in animal and human tissues. Humans are primarily exposed to methylmercury after consuming contaminated saltwater or freshwater fish, causing both neurological and developmental damage. People who regularly and frequently eat highly contaminated fish (or large amounts of moderately contaminated fish) and women of childbearing age are the most likely to be at risk from mercury exposure.

EPA action, industry compliance

The EPA has undertaken numerous measures in recent years to significantly reduce mercury emissions from all major sources. When fully implemented, these actions will reduce total mercury air emissions in the US by nearly 50% from 1990 levels. With more stringent EPA-mandated mercury emission regulations on the horizon, industry will face compliance (to be in place by December 2007) by implementing control methods and related levels of controls for emissions. Raw materials used by industry (especially the use of coal by power plants) will undergo intense analysis in order to be classified by their mercury levels.

Mercury is present in coal in low concentrations - approximately 0.1 ppmw[1]. Typical mercury concentrations found in raw coal used for power plant combustion vary according to the geographical location of the coal seam from which the coal was excavated[2]. Mercury is extremely volatile during coal combustion. In the combustion zone of a coal-fired power plant, mercury is volatilised as elemental

Table 1(a). The following five samples of NIST SRM 1630a (coal) and NIST 1633b (fly ash) were first analysed with the AMA254 as per ASTM Method D-6722. Each set was weighed into small nickel boats that were pre-baked at 400 ˚C.

Sample	Weight (g)	Hg (ng)	Hg (ppm)
NIST 1630a coal (as is) (certified value: 0.081 ± 0.02 ppm)	0.0810	6.5	0.080
	0.0807	7.0	0.087
	0.0813	6.2	0.077
	0.0800	6.6	0.083
	0.0818	6.1	0.074
		Avg (ppm)	**0.080**
		Std	**0.005**
		RSD	**6.3%**
Sample	**Weight (g)**	**Hg (ng)**	**Hg (ppm)**
NIST 1633b fly ash (certified value: 0.141 ± 0.02 ppm)	0.0610	8.9	0.145
	0.0610	8.7	0.143
	0.0608	9.2	0.152
	0.0608	9.6	0.157
	0.0601	8.9	0.147
		Avg (ppm)	**0.149**
		Std	**0.006**
		RSD	**3.8%**

Table 1(b). After calibration, the AMA254 was then ready to analyse two sets of non-certified coal samples.

Sample	Weight (g)	Hg (ng)	Hg (ppm)
Coal #1 (as is)	0.0850	10.0	0.118
	0.0815	8.7	0.107
	0.0858	9.0	0.105
	0.0854	10.0	0.117
	0.0859	9.9	0.115
		Avg (ppm)	**0.112**
		Std	**0.006**
		RSD	**5.4%**
Sample	**Weight (g)**	**Hg (ng)**	**Hg (ppm)**
Coal #2 (as is)	0.0855	24.9	0.291
	0.0863	24.1	0.280
	0.0872	23.8	0.273
	0.0847	26.7	0.315
	0.0862	23.5	0.273
		Avg (ppm)	**0.286**
		Std	**0.018**
		RSD	**6.3%**

mercury, yielding vapour concentrations ranging from 1 - 20 ppbw[1].

The solution

The AMA254 is one instrument that can be used to assist power plants in determining amounts of mercury in raw coal.

The analyser is a unique atomic absorption spectrometer that is specifically designed to determine total mercury content in various solids and liquids, without sample pre-treatment or sample pre-concentration. This instrument is a cost-effective alternative to mercury determination techniques such as oxygen bomb combustion, CVAAS, or ICP, and easily analyses samples to comply with current EPA Method 7343: *Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry*, and recently approved ASTM Method D-6722: *Total Mercury in Coal and Combustion Residues*.

How it works

Designed with a front-end combustion tube that is ideal for the decomposition of difficult matrices such as coal, combustion residues, soils and fish, the operation of the AMA254 may be separated into three phases during any given analysis:

- Decomposition.
- Collection.
- Detection.

The first stage of an analysis is known as the 'decomposition phase'. During this phase, a sample container with a nominal amount of the matrix is placed inside a pre-packed combustion tube. The combustion tube, heated to approximately 750 ˚C through an external coil, provides the necessary decomposition of the sample in a gaseous form. The evolved gases are then transported (via an oxygen carrier gas) to the other side of the combustion tube. This portion of the tube, pre-packed with specific catalytic compounds, represents the area in the instrument where all interfering impurities (i.e. ash, moisture, halogens, and minerals) are removed from the evolved gases.

Following decomposition, the cleaned, evolved gas is transported to an amalgamator for the 'collection phase'. The amalgamator, a small glass tube containing gold-plated ceramics, collects all of the mercury in the vapour. With a strong affinity for mercury and a significantly lower temperature than the decomposition phase, the amalgamator is heated to approximately 900 ˚C, thereby releasing all mercury vapor to the detection system.

The released mercury vapour is transported to the final phase of the analysis, the 'detection phase'. During this phase, all vapors pass through two sections of an apparatus known as a cuvette. The cuvette is positioned in the path length of a standard atomic absorption spectrometer. The spectrometer uses an element-specific lamp that emits light at a wavelength of 253.7 ηm. This wavelength is specific to elemental mercury and will be absorbed by the mercury particles in the vapour for subsequent detection by a silicon UV detector.

Operating software

The AMA254 is equipped with efficient, new Windows® 2000-based operating software, QuickSilver. This software package rapidly determines mercury concentration by integrating the area associated with the total mercury signal vs. time. Quickly performing statistical analyses, QuickSilver features easy-to-use icons and spreadsheet formats for improved user interaction. Real-time diagnostics are used on internal components, and an on-board help manual provides relevant information quickly and easily. The software allows users to define methods and standards; as well as to log in, modify, and perform simple instrument calibrations. QuickSilver also allows the AMA254 to easily interact with peripheral items such as balances, printers and an autoloader.

Conclusion

Research has shown that the AMA254 has the ability to meet and exceed some of the most stringent EPA regulations for the determination of total mercury in coal and combustion residues.

References

1. SENIOR, C.L., 'Behavior of Mercury in Air Pollution Control Devices on Coal-Fired Utility Boilers', 2001, p. 2.
2. 'Ask a Scientist'©, *Argonne National Laboratories*, University of Chicago Newton BBS , Chemistry Archive webpage.