Sampling technologies and air pollution control devices for gaseous and particulate arsenic: A review

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Abstract

Direct measurement of arsenic release requires a good sampling and analysis procedure in order to capture and detect the total amount of metals emitted. The literature is extensively reviewed in order to evaluate the efficiency of full field-scale and laboratory scale techniques for capturing particulate and gaseous emissions of arsenic from the thermo-chemical treatment of different sources of arsenic. Furthermore, trace arsenic concentrations in ambient air, national standard sampling methods and arsenic analysis methods are considered. Besides sampling techniques, the use of sorbents is also reviewed with respect to both approaches (1) to prevent the metals from exiting with the flue gas and (2) to react or combine with the metals in order to be collected in air pollution control systems. The most important conclusion is that submicron arsenic fumes are difficult to control in conventional air pollution control devices. Complete capture of the arsenic species requires a combination of particle control and vapour control devices.

Keywords: Arsenic; Sampling; Air pollution control device; Gaseous emissions; Particulate emissions; Literature review

1. Introduction

Since thermal processes that use arsenic containing sources inherently lead to volatilisation of arsenic, appropriate arsenic capturing devices have to be installed or arsenic capturing methods have to be applied. These devices are said to be commercially available, but very few successful tests have been carried out on industrial scale for the specific case of thermal conversion of chromated copper arsenate (CCA)-treated wood. In the frame of a study that aims at identifying the best available thermochemical conversion technology (pyrolysis, gasification or (co-)combustion) for CCA impregnated wood waste (Helsen and Van den Bulck, 2005), the literature is critically reviewed with respect to the available sampling methods and air pollution control devices for gaseous and particulate arsenic.

Pyrolysis of wood is known to lead to very specific submicron aerosol fumes. Standard methods for emission sampling were found to be not appropriate for pyrolysis effluents (Lachenal et al., 1989). Rapid cooling of pyrolysis gases (heavy tar-like hydrocarbons) quickly clogs the sampling line. Moreover, most experimental studies with CCA-treated wood report arsenic mass balances that are far below 100% (Pasek and McIntyre, 1993; Hirata et al., 1993; Tauw Infra Consult, 1987; Lindroos, 1999). These low mass balances are suspected to be due to incomplete sampling of the metals released.

Since the information available with respect to sampling of arsenic released in a thermal treatment plant for CCA-treated wood is rather limited, industrial experience with other feedstock can be helpful in the design of an appropriate arsenic sampling device or the
application of an appropriate arsenic capturing method. Coal combustion, waste incineration and metallurgical operations generate hot flue gases containing As. Therefore, the literature is critically reviewed with respect to all sampling procedures and air pollution control devices for gaseous and particulate arsenic, regardless of the original feedstock used. It should be kept in mind that CCA-treated wood contains a thousand times more arsenic than for example coal does and thermal conversion of wood may give rise to sticky tar compounds. The detailed description of the mechanisms responsible for arsenic release during thermal conversion of arsenic containing feedstock falls beyond the scope of the present paper, but can be found elsewhere (Helsen et al., 2003a).

When discussing arsenic sampling technologies and air pollution control devices, the measurement of trace arsenic concentrations in ambient air, national standard sampling methods and arsenic analysis methods should also be looked at since they often appear in national or international emission legislation aimed at controlling the air quality.

This paper is organised as follows: in the next section an extensive literature review concerning sampling methods and air pollution control devices for gaseous and particulate arsenic is given, while in the final section the most important conclusions are summarised.

2. A critical literature review

Direct measurement of arsenic release requires a good sampling and analysis procedure in order to capture and analyse the total amount of metals emitted. Therefore, the literature is extensively reviewed with respect to sampling techniques for gaseous and particulate arsenic, as well as capturing methods for arsenic. This literature review is divided into five subsections: CCA-treated wood, other feedstock, trace arsenic concentrations in ambient air, arsenic analysis, and national standard methods.

2.1. CCA-treated wood

Thermal conversion of CCA-treated wood leads to percentages of arsenic volatilised ranging between 8% and 95% of the arsenic content in the wood waste, depending on the reactor temperature, the residence time at a given temperature, the air flow rate, the oxygen partial pressure, the pressure, the extended period of ash heating, the chlorine and sulfur content and the impregnation process (Dobbs et al., 1978; Wilkins and Murray, 1980; Kramer et al., 1985; McMahon et al., 1985; Tauw Infra Consult, 1987; Marutzky, 1990; Hirata et al., 1993; Pasek and Mehtnyre, 1993; Kitamura and Katayama, 2000; Syrjanen and Kangas, 2001; Hata et al., 2003; Helsen and Van den Bulck, 2003).

Combustion trials (Lindroos, 1999) performed with CCA-treated wood in an existing incineration plant, where the normal gas cleaning system is extended with a venturi scrubber, show that the arsenic emission is too high (2.8 mg Nm⁻³). Furthermore, the use of electrostatic precipitators (ESP) does not suffice to keep arsenic emission below the European target value of 0.5 mg Nm⁻³ (for the sum As + Cr + Cu + Sb + Pb + Co + Mn + Ni) (Lindroos, 2002). It was concluded that a special design is needed for the gas cleaning, usually a combination of wet and dry methods. The latter have the disadvantage that as far as occupational hygiene is concerned, the treatment of dry impure arsenic trioxide dust is difficult. Scrubbing of the gases is said (Syrjanen, 1999) to be of special importance since most of the arsenic (60–90%) is released as very small particles. However, venturi scrubbers are generally not efficient in capturing small particles (1 μm in diameter or less) (Barton et al., 1992).

Wu et al. (Wu and Biswas, 1993; Wu et al., 2000; Wu and Barton, 2001; Iida et al., 2004) proposed the introduction of mineral sorbents in the combustion system as a solution for both the problem of metal emission and the problem of metal leaching from the combustion ash. Equilibrium analyses (Wu and Barton, 2001; Iida et al., 2004) were conducted to predict potential sorbent materials for chemically adsorbing the heavy metals during the combustion of CCA wood. Alkaline earth metals and alkali metals were found to be effective for capturing arsenic by forming metal-sorbent compounds. However, sulfur and chlorine present in the combustion system may interfere with the performance of the sorbents due to the formation of chlorides and sulfates that deplete available sorbent for the metals. Ca(OH)₂ and Na₂CO₃ were then examined in an experimental combustion system for their performance (Iida et al., 2004). The addition of these sorbents significantly enhanced the retention of the metals in the ash, especially for arsenic. Regarding the leaching Ca(OH)₂ was shown to be very effective, except for chromium, while Na₂CO₃ resulted in very high leaching levels of all metals. The changes in retention and leaching are due to the formation of new metal-sorbent compounds.

A lot of combustion experiments with CCA-treated wood were performed on lab-scale, the resulting mass balances for arsenic never reaching 100%. Five of these studies, each using different sampling systems, are listed in Table 1. Helsen et al. (2003b) developed a sampling and analysis method for arsenic emissions during pyrolysis of arsenic containing wood on lab-scale. Validation was carried out through tube furnace experiments using both CCA-treated wood and arsenic trioxide powder as input. For the working conditions considered (pyrolysis at 350 °C for 20 min with a nitrogen flow rate of 100 Ni h⁻¹) the combination of a quartz cooling tube and a cellulose ester membrane filter impregnated with
Table 1
Overview of combustion experiments with CCA-treated wood performed on lab-scale, with their corresponding flue gas cleaning equipment and resulting arsenic mass balance

<table>
<thead>
<tr>
<th>Reference</th>
<th>Flue gas cleaning equipment</th>
<th>As mass balance</th>
</tr>
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<tbody>
<tr>
<td>Taw Infra Consult, 1987</td>
<td>Multicycle+cellulose nitrate filter</td>
<td>&lt;50%</td>
</tr>
<tr>
<td>Pasek and McIntyre, 1993</td>
<td>Two bubblers: empty + 2% NaOH or glass beads + 2% monoethanolamine</td>
<td>20–90%</td>
</tr>
<tr>
<td>Cornfield et al., 1993</td>
<td>Glass fibre filter + 5 washing bottles NaOH 0.1 M</td>
<td>NA</td>
</tr>
<tr>
<td>Hirata et al., 1993</td>
<td>Three spiral traps, chilled with ice water (0 °C), dry ice-methanol (−60 °C) and liquid N2 (−190 °C)</td>
<td>50–80%</td>
</tr>
<tr>
<td>McMahon et al., 1985</td>
<td>Glass transfer tube + glass fibre filter + TBAH impregnated cellulose filter</td>
<td>61–104%</td>
</tr>
</tbody>
</table>

NA. As mass balance is not available (non-significant amount captured in washing bottles and the metals retained were all in particulate form); TBAH, tetra-n-butylammonium hydroxide.

A Na2CO3—glycerol solution was sufficient to capture the arsenic. Two extra impingers (the first one containing 50 ml HNO3 1 M in the case of CCA-treated wood and 50 ml NaOH 0.1 M in the case of As2O3 and the second one containing 50 ml NaOH 0.1 M) were added downstream of the filter section as backup either in case of filter failure or to check whether all the arsenic released is captured by the cooling tube and filter. The arsenic distribution over the different units of the sampling train was determined by inductively coupled plasma mass spectrometry (ICP-MS), after dissolving the filters and backup pads in HNO3 and H2O2.

Characterisation of the resultant combustion ash or charcoal residue has been performed by Helsen and Van den Bulck (1998), Hata et al. (2003) and Iida et al. (2004) by scanning electron microscopy coupled to energy dispersive X-ray analysis (SEM-EDX), transmission electron microscopy (TEM) or X-ray diffraction (XRD). Both Cu arsenates and Cr arsenates have been identified.

It can be concluded that additional investments are needed for better gas cleaning systems, tuned in to the type of burner, gasifier or pyrolyser, and for measurements to control emissions.

2.2. Other feedstock

2.2.1. Arsenic oxide

In commercial installations particulate matter is often separated at an elevated temperature (circa 200 °C) at which other impurities, such as arsenic oxide, are appreciably volatile. Wouterlood and Bowling (1979) studied the removal of arsenic oxide vapour from hot flue gases on the laboratory scale, by passing the gas stream through a bed of different adsorbent particles. Physical methods seem attractive because arsenic oxide is a known catalyst poison, which implies that it is strongly and selectively adsorbed on particulate surfaces. Inert materials such as glass beads, glass wool, and fly ash were found to be virtually ineffective; basic and acid chemicals worked to a limited extend. Surface-active agents such as activated carbons, silica gel, and molecular sieve 13X adsorbed arsenic oxide vapour strongly.

In an attempt to capture the particulate and volatile arsenic compounds at the same time, Walsh et al. (1977) tested an impregnated filter sampling system. An aqueous glycerol and polyethyleneimine polymer solution was used to impregnate Whatman filters. Laboratory studies showed that for volatile arsenic trioxide the total collection efficiency of three impregnated filters in line averages approximately 96% at flow rates from 15 to 23 l min⁻¹. Preliminary test results indicated that tetra-n-butylammonium hydroxide (TBAH) is apparently a very efficient collection substrate for arsenic trioxide vapours. The efficiency of filter sampling for arsenic in the atmosphere has also been studied by Appel et al. (1984) by comparing glass fibre filters, Teflon filters and cellulose filters impregnated with TBAH. Only the impregnated filters provided measurable As levels, but still not a 100% collection.

While multiple species of inorganic arsenic (particulate form, arsenic trioxide vapour and arsine) coexist in industrial environments, traditional air sampling methods quantify only total inorganic arsenic. The National Institute for Occupational Safety and Health (NIOSH) conducted laboratory experiments and field studies to develop a technique to separate mixtures of particulate inorganic arsenic compounds and arsine, and to detect and quantify arsenic trioxide vapour (Costello et al., 1983). This study concluded that in the presence of heated arsenic sources, such as battery manufacturing plants, monitoring solely with conventional (untreated) filters will underestimate arsenic exposure because arsenic trioxide vapour is not efficiently collected. Furthermore, the individual particles collected on the filters were spherically shaped with a median circular area equivalent diameter less than 1 μm. Arsenic was not detectable in these particles, indicating that the arsenic concentration in the particles was less than 1% of the total mass.

Demange et al. (1992) studied the efficiency of several filters and concluded that different methods perform well as long as impregnated filters are used. They developed a sampling train consisting of a prefilter to retain particulates and As2O3 vapour, followed by two quartz fibre filters to trap arsine (Demange et al., 2000).
The prefilter was a quartz fibre filter impregnated with sodium carbonate. The successive quartz fibre filters were impregnated with silver nitrate. The filters were dissolved in nitric acid, prior to analysis by ICP atomic emission spectrometry (ICP-AES).

2.2.2. Other arsenic containing wastes

On an industrial scale arsenic containing wastes are incinerated in a rotary kiln incinerator (for example at the waste treatment company INDAVER in Belgium). The gas cleaning equipment consists of a combination of a boiler (for heat recovery), an electrostatic precipitator, a four-steps wet scrubber (using lime and sodium hydroxide) and an injection of activated carbon or brown coal. The percentages of arsenic retained in the different units are presented in Table 2 (Wauters, 1998). From Table 2 it is clear that an efficient filter (electrostatic precipitator) does not succeed in capturing all the arsenic. Circa 5.4% of the As originally present in the waste passes the electrostatic filter and is captured in the wet scrubber by absorption and/or chemisorption. It is not known, however, whether the percentages of arsenic retained in the different units would be the same or totally different if the As content in the waste stream is much higher, for example when CCA-treated wood is used as input.

An arsenic closure problem is often seen in medical waste incinerators, fed with arsenic containing waste in the form of operating and delivery room materials such as cloth, blue plastic and rubber items and sterilisation wrap. A study conducted in a rotary kiln incinerator by the U.S. EPA showed the total mass balance of arsenic ranging from 38% to 73% of the input arsenic material (Chesworth et al., 1994). Chesworth et al. (1994) used a co-flow laminar diffusion flame system to study the fate of arsenic and found that the arsenic species, predominantly in aerosol form, are captured by a Gore-tex filter, which may act as a condensation surface for species during sampling.

Hinshaw (1994) studied the behaviour and control of metals in a hazardous waste incinerator using synthetic wastes spiked with for example concentrated As$_2$O$_3$ aqueous solution. By using an air pollution control system, consisting of a spray dryer, a cooler/condenser, a venturi scrubber, a baffle absorber and a mist eliminator, the metal stack emission rate was highly dependent on the differential pressure across the venturi scrubber, but less dependent on the chlorine feed concentration. However, the behaviour and control of the metals in the gases entering the air pollution control system was highly sensitive to the chlorine level.

Venkatesh et al. (1996) evaluated various mineral sorbents constituting a spectrum of alumino-silicate compounds and attapulgite clay (a magnesium hydroxide silicate compound) for retention and immobilisation of arsenic and other heavy metals. A mixture of the mineral sorbent, PVC powder (to examine the influence of chlorine) and metals spike (200 mg As/kg, added as arsenic oxide) was incinerated and the resultant solid product was analysed for metal retention and leachability. Combining the dual criteria of limiting metal vaporisation and reducing leachability, and the additional criteria that the toxicity characteristic leaching procedure (TCLP) extract metal concentrations be below regulatory levels, kaolin and attapulgite clay appear to have the most potential as sorbents.

2.2.3. Coal

Coal combustion is estimated to account for 2–5% of the total arsenic emissions from anthropogenic sources globally (Sterling and Helble, 2003). The vapourised arsenic will ultimately partition between the vapour phase and the particulate fly ash, which leads to the enrichment of arsenic in the smallest particles. Aside from its potential to be a hazardous air pollutant if emitted to the atmosphere, arsenic, in the form of gaseous arsenic oxide (As$_2$O$_3$), is poisonous for selective catalytic reduction (SCR) catalyst; therefore, its presence is detrimental to the operation of SCR units for NO$_x$ control. As$_2$O$_3$ solidifies on both active and non-active sites in the vanadium-based catalysts that are used in SCRs, which reduces the activity of the catalyst. Electrostatic precipitators (ESPs) are often used to capture the fly ash in the flue gas. However, the ESP is usually installed after the SCR unit and therefore does not offer a solution for the catalyst poisoning problem. The 80% capture rule-of-thumb, which assumes that each row of the ESP collects circa 80% of the fly ash in the flue gas entering the row, is a common assumption in the utility industry. The actual collection efficiency will vary according to many variables, such as combustion conditions, and ash amount and type. Sakulpitakphon et al. (2003) found that the fly ash arsenic content seems to be within the range of the feed coal arsenic content, which suggests that most of the arsenic is captured on fly ash. The arsenic concentration in the fly ash increases

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Arsenic (%) retained in the different parts of the INDAVER rotary kiln incineration plant (Wauters, 1998)</th>
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</thead>
<tbody>
<tr>
<td>Collected in</td>
<td>Bottom ash</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>Rotary kiln</td>
</tr>
<tr>
<td>As (wt%)</td>
<td>14.6</td>
</tr>
</tbody>
</table>
markedly with decreasing particle size (Davison et al., 1974; Maenhout et al., 1993). This dependency on particle size is explained by a mechanism involving high temperature volatilisation followed by preferential condensation or adsorption onto the smallest particles. Since thermodynamic equilibrium calculations do not take into account the formation of small particles (difficult to collect fume), nor kinetic effects, maximum theoretical removals are calculated (Frandsen et al., 1997; Blander et al., 1998; Sandelin and Backman, 2001). However, in a system of multiple metals, thermodynamic equilibrium analysis may identify the dominant forms of the metallic and radical species, which can provide useful information in the development of more accurate kinetic models (Wu and Biswas, 1993).

Sorbent injection is a very attractive method to reduce arsenic emission during coal combustion (Gullett and Raghunathan, 1994; Jadhav and Fan, 2001; Wu and Barton, 2001; Sterling and Helble, 2003). The most important sorbents studied with respect to their effectiveness to reduce arsenic emissions during coal combustion are summarised in Table 3. Arsenic reacts, while still in the vapour state, at high combustion temperatures, with various sorbents to form larger particles that can be collected effectively by particulate collection devices. The sequestering action of the sorbents reduces the vapour form and/or fine particle form of the metal (Gullett and Raghunathan, 1994). These sorbents can be fly ash, activated carbon or mineral material. Hydrated lime (Ca(OH)₂) and limestone (CaCO₃) are found to be very effective. While Ca is responsible for the reaction of As with these solids, it is the availability of active Ca sites at the surface of these solids that determines the rate of reaction (Sterling and Helble, 2003). At temperatures below 600 °C tricalcium orthoarsenate (Ca₃As₂O₇) is formed, while temperatures between 700 and 900 °C give rise to the formation of dicalcium pyroarsenate (Ca₂As₂O₇), which is unstable and therefore responsible for a decrease in As capture at higher temperature (Jadhav and Fan, 2001). Sterling and Helble (2003), however, reported a maximum capture of As with calcium oxide at 1000 °C. They concluded that any calcium present in fly ash can react with arsenic oxide vapour and capture the metal in water-insoluble forms of the less hazardous As(V) oxidation state. Seames and Wendt (2000) suggest the formation of As–Ca reaction products in supermicron particles in the post-combustion zone. Co-combustion of municipal sewage sludge with coal allows the arsenic to be reactively scavenged by calcium (Seames et al., 2002). Coal alone contained insufficient calcium to accomplish this same scavenging effect.

### 2.2.4. Copper ores

In the metallurgic industry, the purification of copper ores also results in the volatilisation of arsenic. Since the aim of this purification process is to eliminate as much arsenic as possible to obtain a pure copper product, the release of arsenic to the gas phase (and subsequent capture) is highly favourable. The company Umicore (Olen, Belgium), for example, makes use of a gas cleaning system consisting of a combination of a boiler (for energy recovery), injection of lime, injection of activated carbon or brown coal, dilution with air until the final temperature has reached 95 °C and a baghouse filter. The arsenic distribution over the different units is not known, but the resulting arsenic concentration in

### Table 3

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sorbent</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Sterling and Helble, 2003</td>
<td>Ca compounds in fly ash: CaO, 2CaO·SiO₂, CaO·SiO₂</td>
<td>CaO is most effective (T: 600–1000 °C). Reaction product is Ca arsenate.</td>
</tr>
<tr>
<td>Jadhav and Fan, 2001</td>
<td>Activated carbon Minerals: lower affinity to adsorb As</td>
<td></td>
</tr>
<tr>
<td>Wu and Barton, 2001</td>
<td>Al-, Fe-, Li-, Na-, K-, Be-, Mg-, Ca-based sorbents</td>
<td>Effectiveness may be reduced when Cl or S is present.</td>
</tr>
<tr>
<td>Gullett and Raghunathan, 1994</td>
<td>Hydrated lime Limestone Kaolinite Bauxite</td>
<td>As capture is function of sorbent type and injection mode (1000–1150–1300 °C): kaolinite &gt; limestone &gt; hydrated lime. Not a simple condensation mechanism, the particles’ external surface area or pore diffusion is important to the capture mechanism.</td>
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**Notes:**
- **Reference:** Sterling and Helble, 2003
- **Sorbent:** Ca compounds in fly ash: CaO, 2CaO·SiO₂, CaO·SiO₂
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- **Sorbent:** Activated carbon Minerals: lower affinity to adsorb As
- **Reference:** Wu and Barton, 2001
- **Sorbent:** Al-, Fe-, Li-, Na-, K-, Be-, Mg-, Ca-based sorbents
- **Comments:** Effectiveness may be reduced when Cl or S is present. Products with high alumina content: low leaching. High silica content: high leaching.
- **Reference:** Gullett and Raghunathan, 1994
- **Sorbent:** Hydrated lime Limestone Kaolinite Bauxite
- **Comments:** As capture is function of sorbent type and injection mode (1000–1150–1300 °C): kaolinite > limestone > hydrated lime. Not a simple condensation mechanism, the particles’ external surface area or pore diffusion is important to the capture mechanism.
the exhaust gas is around 0.47 mg Nm$^{-3}$, which is below the limit specified in the emission legislation (1 mg Nm$^{-3}$). This low concentration is reached by the addition of lime, the presence of a thin dust layer on the filter and mixing the gas stream with air, resulting in a dilution. However, the absolute amount of arsenic emitted into the atmosphere is significant (295.6 kg year$^{-1}$) (Geenen, 1999). The amount of arsenic collected in the dust reached 745 kg in 1998 (VMM, 1998). Chemical analysis of copper smelter flue dust reveals the presence of arsenite (As(III)), arsenate (As(V)), arsenic sulfide and As$_2$O$_3$ (Eatough et al., 1979).

In metallurgical processes arsenic disposal is shifted from formation of calcium arsenate to formation of insoluble ferric arsenate compounds. Lime precipitation, which was widely used in the past, is being abandoned as a result of strong evidence showing that calcium arsenate compounds decompose slowly in contact with atmospheric CO$_2$ to form calcium carbonate and soluble arsenic acid. Scorodite (FeAsO$_4$·2H$_2$O) has several advantages over arsenical ferrihydrite as a disposal compound including a lower iron demand, a higher density and a greater thermodynamic stability (Riveros et al., 2001).

At the copper line of Outokumpu Harjavalta Metals (Pori, Finland), which is the major copper producer in Finland and manufacturer of CCA preservatives, a trial has been carried out to recycle CCA-treated timber in the copper smelting process. The energy content of the wood was used in the flash smelting process, copper and arsenic were recovered in the CCA preservative manufacturing plant, burning gases were fed to the sulphuric acid plant and chromium is subjected to a slag treatment process. How the arsenic was recovered is not specified (Nurmi and Lindroos, 1994). A second trial investigates heavy metal emission during gasification of CCA-treated wood and subsequent combustion of the synthesis gas for district heating (Nurmi, 1996). The arsenic emission varied between 1120 and 1640 mg h$^{-1}$, corresponding to 63–92 g of As for a 56 h run, being at maximum 0.1% of the arsenic originally present in the wood. The amount of arsenic collected in the condensing water and the demister were respectively 14.2 kg and 30 g, while 8.8 kg of As remained in the ash. However, the arsenic mass balance is less than 30%, illustrating again that accurate sampling of arsenic is not an easy job.

2.3. Trace arsenic concentrations in ambient air

A variety of sampling and analytical techniques have been used to measure trace metal concentrations in air including impingers, electrostatic precipitators and filters. Some sampling techniques used to measure trace metal (in particular As) concentrations in ambient air are listed in Table 4, together with their efficiencies. Filter efficiencies seem to decrease if lower arsenic concentrations have to be measured.

Smith (1979) derived an equation to calculate the overall efficiency of a sampling train consisting of a series of impingers. He concluded that the amount caught by the last impinger should be close to zero to obtain a high overall efficiency. The presence of sample in the last impinger indicates that some unknown amount has passed through the train entirely. Smith emphasised the need to seek the sampling conditions and train length that will produce a nil indication in the last impinger. Li and Pupp (1979) investigated the efficiency of water as a collection medium for arsenic oxide vapour. They concluded that water and dilute (2%) sodium hydroxide are equally effective collection media for arsenic trioxide vapour. Three Greenburg-Smith impingers, each filled with 250 ml of water, cooled with ice, are satisfactory for the collection of arsenic trioxide vapour. No vapour was lost from such a sampling train at flow rates up to 20 l min$^{-1}$. However, up to 15% of the collected arsenic may be absorbed on the walls of the impinger train; this amount will not dissolve in water unless the train is thoroughly washed with sodium hydroxide.

Over recent years, filters have been favoured over other measurement methods due to their high efficiency for collection of small particles (Maggs, 2000). Different filter media have been considered for the determination of trace metals in air, such as glass fibre, quartz fibre, membrane filters and Teflon filters. An important consideration in selecting the most appropriate filter medium for collection of trace elements in particulate matter is the background metal concentration of the filter material (blank value). The blank values of arsenic in the different filter media are given in Table 5, together with some other properties.

Impregnated filters are found to be able to capture simultaneously both particulate arsenic and arsenic oxide vapour. The latter is collected by reaction with the chemical agent on the impregnated filter, e.g. for a sodium carbonate impregnated backup pad (Maggs, 2000) the following stoechiometric reaction takes place:

\[
\text{As}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaAsO}_2 + \text{CO}_2
\]

2.4. National standard methods

Besides the American NIOSH standards (NIOSH, 1984, 1985) and the MDHS 41/2 (MDHS, 1995) for the sampling of arsenic in air (see Table 4), a German standard VDI 3868 (VDI, 1994) and a Dutch draft NVN 2817 (NNI, 1996) have been published. The German standard has been developed to sample the total amount of particulates and filter passing matter (metals, metalloids and their compounds), while the Dutch draft describes a sampling and analysis method for the
determination of the content of the elements arsenic, cadmium, chromium, copper, mercury, lead, zinc and their alloys, in particulate matter and in the gas phase (sampling fume, process and exhaust gases). Both methods extract a part of the gas volume isokinetically from the exhaust stream and force this part through a two-stage device, comprising a filter system that retains the particulate matter and an absorption system in the form of washing bottles. At least three gas washing bottles are connected in series and filled with suitable absorbent solutions. Different (untreated) filter materials and different absorbent solutions can be used. Metal analysis is performed by using hydride generation atomic absorption spectrometry (AAS) or oven AAS in the case of VDI and AAS or inductively coupled plasma atomic emission spectrometry (ICP-AES) in the case of NVN. As a control the last washing bottle is analysed separately; the amount of arsenic found in this bottle should be less than 10% of the total mass. Using the VDI standard there have been made positive experiences with a series of waste incinerators and furnaces using fossil fuels.

The U.S. EPA Reference Methods (EPA, 1993) have been set up to provide industry with a reasonable and reliable means of demonstrating compliance with applicable regulations. Among them are U.S. EPA Method 108 for the determination of particulate and gaseous arsenic emissions and U.S. EPA Method 108A for the determination of arsenic in ore samples from non-ferrous smelters. According to the U.S. EPA Method 108 particulate and gaseous arsenic emissions are withdrawn isokinetically from the exhaust stream and force this part through a two-stage device, comprising a filter system that retains the particulate matter and an absorption system in the form of washing bottles. At least three gas washing bottles are connected in series and filled with suitable absorbent solutions. Different (untreated) filter materials and different absorbent solutions can be used. Metal analysis is performed by using hydride generation atomic absorption spectrometry (AAS) or oven AAS in the case of VDI and AAS or inductively coupled plasma atomic emission spectrometry (ICP-AES) in the case of NVN. As a control the last washing bottle is analysed separately; the amount of arsenic found in this bottle should be less than 10% of the total mass. Using the VDI standard there have been made positive experiences with a series of waste incinerators and furnaces using fossil fuels.

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membrane or glass fibre filters, and Method 804 “As, Se and Sb in urine and air by hydride generation and AAS” using membrane filters for the air samples.

The International Standards Organisation (ISO) is engaged in the development of ISO 15202, which will describe a generic method for the determination of metals and metalloids in airborne particulate matter by ICP-AES (Butler and Howe, 1999). However, an international standard method for the determination of gaseous and/or particulate arsenic in emitted gas/aerosol streams has not yet been developed.

2.5. Arsenic analysis

In dust analysis, the analytical step is generally preceded by an appropriate preparation of the sample in order to dissolve the collected particulate matter or extract the metals to be analysed. The dissolution can be achieved by wet digestion (ultrasonic agitation, hot-plate digestion or microwave assisted) or dry ashing. There is risk of losing part of the metal and/or contaminating the sample solution if the number of intermediary stages in the extraction process increases. Alternative sample introduction systems could be: laser ablation (LA) or electrothermal vaporisation (ETV). After dissolution, analysis is carried out using a number of different techniques: ion chromatography (IC), ultraviolet spectrometry (UV), electrochemical methods (EQ) such as differential pulse polarography, atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), laser plasma atomic emission spectrometry (LP-AES) and X-ray fluorescence spectrometry (XRF). Both the minimum detection limit (determined as that concentration which produces a signal equivalent to 2 or 3 times the standard deviation of the blank signal for aqueous solutions) and the relative error (based on the analysis of standards) are important characteristics of the analytical technique.

Analysis of the solid product resulting from the thermal process (charcoal or ash) is usually performed by one of the following methods: X-ray diffraction (XRD), electron spectroscopy for chemical analysis (ESCA), scanning electron microscopy coupled to energy dispersive X-ray analysis (SEM-EDX), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), electron spin resonance spectroscopy (ESR), particle induced X-ray emission (PIXE), electron induced X-ray emission (EIXE) or neutron activation analysis (NAA).

A detailed description and comparison of these analytical techniques is beyond the scope of the present paper. Good reviews have been made by Burguera and Burguera (1997) and Vanhaecke and Moens (1999), who described trends in trace element determination and speciation. Since trivalent arsenic is considerably more toxic than pentavalent arsenic, speciation studies are very important.

3. Conclusions

From the literature review the following conclusions are drawn:

1. A simple cooling and/or condensation process does not succeed in collecting all the arsenic.
2. Since most of the arsenic is released as very small particles, venturi scrubbers are generally not efficient in capturing arsenic.
3. Physical methods (adsorption on particulate surfaces) seem attractive but only surface-active agents, such as activated carbons, silica gel, and molecular sieves, adsorb arsenic oxide vapour strongly.
4. Filtration through a quartz fibre, glass fibre or Teflon filter collects the arsenic only partly; for Nuclepore and Millipore filters, on the other hand, high filter efficiencies were reported; good collection efficiencies were reported for alkali impregnated (cellulose ester membrane) filters; impregnation (with an aqueous glycerol-polyethylenimine solution, sodium carbonate or TBAH) seems to be necessary, resulting in a chemical reaction between the arsenic compound and the chemical agent on the filter.
5. The lower the arsenic concentration to be measured (e.g. low concentrations in the ambient air), the lower the filter efficiency.
6. Also the combination of filters and impingers (containing acids or alkali) seems to be efficient.
7. Water and dilute sodium hydroxide are equally effective collection media for arsenic trioxide vapour in impingers; however, some arsenic compounds adsorbed to the impinger walls need to be thoroughly washed with sodium hydroxide.
8. In the case of a sampling train consisting of a series of impingers, the amount caught by the last impinger should be close to zero to obtain a high overall efficiency.
9. In big chimneys a small part of the total emitted flow is isokinetically sampled and forced through a heated filter and at least three impingers that contain an acid solution.
10. To collect arsine (AsH₃) a charcoal tube or a silver nitrate impregnated filter is used.
11. In coal fired power plants fine fly ash particles that are enriched with arsenic are collected in an ESP; however, ESPs are found to be insufficient to capture all arsenic released when incinerating arsenic containing waste.
12. Sorbent injection combined with filtration is a very attractive and efficient method to reduce arsenic emissions during coal combustion and metallurgical operations; also for the combustion of CCA-treated wood waste this option is under study now.

13. An international standard procedure for sampling and analysis of gaseous and/or particulate arsenic emissions does not exist; only national standards and drafts, such as VDI 3868, NVN 2817, EPA method 108 and NIOSH 7901, can be found.

14. A lot of analysis techniques are available to determine the arsenic content of a sample.

Submicron arsenic fumes are thus difficult to control in conventional particle control devices such as an electrostatic filter or a baghouse, since they have their minimum collection efficiencies in the submicrometer range. Complete capture of the arsenic species requires a combination of particle control and vapour control devices, such as a combination of an efficient filter and a wet scrubber or the injection of a suitable sorbent to trap arsenic vapours (arsenic oxides or arsine). Only if the scrubber solution can be reused in the CCA impregnation process, no additional waste streams are created. The use of sorbents to capture the arsenic vapours by physical and/or chemical means is a very attractive alternative to scrubbers, particularly when the sorbents are able to capture and bind the metals in the bottom ash or charcoal, thereby preventing them from exiting with the flue gas. The sorbents needed for this scavenging effect can also be delivered by other waste streams in a co-combustion plant. Another approach is that the vapourised metals react with the sorbent particles at elevated temperatures or heterogeneously condense onto the sorbents as the flue gas cools. The goal of this approach is to make sorbent particles available in the flue gas, so that metals can react or condense, and effectively be collected by air pollution control systems.

Lab-scale experiments have shown that impregnated filters can collect both particulate arsenic and arsenic oxide vapours simultaneously. However, these impregnated filter systems seem to be not feasible on an industrial scale. For the same reason arsenic toxicants, as recovered in industrial scale. For the same reason arsenic toxicants, arsenic vapours simultaneously. However, these impregnated filters appear mainly in trivalent form. Since (re)-oxidation to the pentavalent form only occurs under high pressure, most of the arsenic released is expected to be in trivalent state (as \( \text{As}_2\text{O}_3 \)), and thus difficult to capture.

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