# MONITORING STACK GAS EMISSIONS OF VOLATILE TRACE ELEMENTS, SULPHUR DIOXIDE AND PM$_{10}$ PARTICULATES FROM COAL-FIRED STOKER SYSTEMS

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## ABSTRACT

A good deal of industrial coal combustion in New Zealand uses low ash highly alkaline sub-bituminous coals on stoker type units for raising process heat - substantially different coals, conditions and requirements for those most commonly used globally. Emissions control is typically by inertial grit arrestors (multicyclones). Emissions of interest include levels of toxic trace volatile inorganics (arsenic, boron, selenium, and mercury) sulphur dioxide and levels of PM$_{10}$ particulates. The need for reliable methodologies for measuring the emissions and the requirement to better understand the factors responsible for them is becoming increasingly important.

This paper presents the results of trace element mass balances from a series of laboratory combustion trials. It also presents comparisons from laboratory combustion trials and from industrial sites of monitoring sulphur dioxide emission levels as measured by standard and non-standard methods, and PM$_{10}$.

The concentrations of boron, arsenic and selenium in flue gas as measured by USEPA Method 29 were low. For boron, an element not specified in the standard but of particular relevance to New Zealand, this was mainly due to the highly alkaline nature of the coal and the firing system used to combust it rather than to inability of the method to trap boron. Boron, arsenic and mercury recoveries were reasonable (greater than 60% recovery) whereas selenium recoveries were often poor (less than 20%). Much of the unaccounted for portions of these elements are thought to have been trapped within ashy deposits throughout the combustion rig.

Agreements between sulphur dioxide concentrations as measured by the standard wet chemical USEPA Method 6 and by the more user friendly non-standard electrochemical and pulsed UV methods are frequently better than 5%. Again the highly alkaline nature of the coal and the firing system used to combust it had a considerable influence on sulphur emission levels with anywhere from 5 to 25% retention in bottom ash being observed.

Total particulate emissions as determined by a six-stage in stack cascade impactor system (USEPA Method 201A) are generally in good agreement with those obtained by a less cumbersome single stage filter method. The percentage PM$_{10}$ material recovered from the single filter is also not widely different from that determined by the impactor but the size distribution of particulates is biased toward the larger sized fractions and do not give a true picture. The mean PM$_{10}$ emission factor (63%) was in good agreement with those cited by the USEPA (55 to 65%) for stoker type firing systems with inertial grit arrestors.

**INTRODUCTION**

Increased public concern relating to the release of potentially harmful emissions from combustion processes at industrial sites is leading to legislation aimed at reducing emissions. The need for reliable methodologies for measuring the emissions and the requirement to better understand the factors responsible for them is becoming increasingly important. Among the targeted emissions are chemical species such as sulphur dioxide and the toxic volatile inorganics arsenic, boron, selenium and mercury [1-3]. Also targeted are particulate emissions - especially those designated as being of less than 10 microns in diameter ($PM_{10}$ particulates) and believed to be sufficiently small to enter the respiratory system and bring about related health problems [4,5].

Coal-fired combustion is accompanied by emissions in each of these areas and it is important, given its significance as a fuel, that its contribution is determined accurately and understood as fully as possible.

In New Zealand, many industrial coals are low ash (3 to 8%) sub-bituminous rank with high levels of calcium (up to 60% CaO in ash may be found). The coals are typically used in stoker, and occasionally fluidised bed, combustion conditions. Given the difference in combustion regimes and the highly alkaline nature of the coal ashes it is possible that sulphur, particulate and trace element emissions and partitioning behaviour may not follow the trends seen in the majority of previous studies. Of particular interest is the trace element boron which is present in moderate to high concentrations in New Zealand coals. In the course of conducting research to quantify and understand the emission levels of these species from New Zealand industrial coals under New Zealand conditions it has been necessary to monitor their emissions on a number of occasions from a number of sites using a variety of monitoring methods.

A great deal of the available data relating to particulate, sulphur and trace element emissions comes from power stations using pulverised bituminous coal- i.e. a high temperature (1250 to 1500°C) combustion regime characterised by fine particles and short residence times. There is less data relating to fluidised bed combustion where the temperatures are lower (800 to 950°C) but residence times are much longer. There is also comparatively little data for stoker systems where intermediate temperatures, long residence times, large particles and comparatively static beds are encountered. In addition most of the data is for cases where the ash generated during combustion is dominated by oxides of silicon, aluminium and iron with comparatively small contributions from the alkaline earth oxides typical of New Zealand coal ashes.

This paper presents and discusses the results of trace element mass balances from a series of laboratory combustion trials, comparisons of sulphur dioxide emission levels as measured by standard and non-standard methods and $PM_{10}$ monitoring from industrial sites.

## EXPERIMENTAL

### Emissions of toxic volatile trace inorganics

To carry out mass balances of toxic volatile inorganics including arsenic, boron, selenium, and mercury, well characterised samples of New Zealand industrial coals were burned on a laboratory scale 50 kW stoker or fluidised bed combustion system. Parameters such as coal feed rate, gas flows and sampling temperatures were closely controlled. After exiting the combustor the exit gases passed over a convective tube bank which controlled the stack sampling temperature. Fly ash was removed by a high efficiency cyclone and the gas then passed through a quartz isokinetic heated sampling train to a quartz disc filter where any remaining particulates were captured. The gas then entered a series of bubblers containing solutions to trap the targeted trace elements using methods similar to that of USEPA Method 29 "Determination of Metal Emissions from Stationary Sources". For arsenic, selenium and boron a solution of 5% nitric acid in 10% hydrogen peroxide was used while for mercury a solution of 4% potassium permanganate in 10% sulphuric acid was used[6,7]. The mercury concentrations in the impinger solutions were measured by cold vapour atomic absorption spectroscopy while inductively coupled plasma mass spectrscopy (ICP-MS) was used for the other elements. After exiting the sample line the gas passed through a desiccant and on to a dry gas meter for volume measurement. The moisture content of the flue gas was determined from the increase in weight of the desiccant and impinger solutions and the concentrations of trace elements calculated in μg per dry standard cubic meter of flue gas.

After each run the bottom ash, cyclone ash and filter ash were recovered, weighed, digested and analysed for trace elements. The sand used as fluidising medium in the fluid bed experiments was also digested and analysed for trace elements.

### Emissions of sulphur dioxide

Environmental authorities frequently specify a wet chemical standard such as USEPA Method 6 "Determination of sulphur dioxide from stationary sources" for measurement of this substance. The process involves the extraction of a gas sample through a teflon lined probe with capture of particulate matter by a filter at the inlet of the probe. The gas is then passed to an impinger containing a solution of 80% isopropanol where any sulphuric acid mist (including sulphur trioxide) is captured. The gas is then passed to two further impingers both of which contain a 3% hydrogen peroxide solution for sulphur dioxide capture. The gas is then passed through a fourth impinger containing silica gel and from there to the dry gas flow measurement equipment. The contents of the second and third impingers are combined and the amount of sulphur dioxide captured determined by barium-thorin titration.

Also available for sulphur dioxide measurement are rigorously tested but non-standard methods such as the German manufactured Testoterm 350 electrochemical cell analyser. This equipment, unlike the standard method, gives immediate and continuous on-line sulphur dioxide emission data and is much easier to operate and less cumbersome than the standard wet chemical method.

Sulphur dioxide measurement was performed by both methods for comparison purposes for some runs carried out both at industrial sites and on the laboratory rig. At exactly the same time as flue gas was being drawn into the Method 6 sampling train, a sample of gas was being drawn from the same sampling port into the Testoterm 350. In this unit the gas was filtered and passed through a heated line to a gas preparation apparatus. Within this apparatus the flue gas was cooled quickly through a Peltier element to remove condensate while preventing absorption and hence loss of sulphur dioxide. The gas then passed to an electrochemical cell specifically chosen for sulphur dioxide measurement. The Testoterm was calibrated against a certified bottled standard gas prior to and after sampling.

For some runs both at industrial sites and on the laboratory rig, sulphur dioxide measurement was performed using both the Testoterm equipment and a pulsed UV fluorescence analyser. For use of this equipment, the flue gas sample was withdrawn from the stack, diluted with inert gas to lower the dew point to below room temperature and passed through teflon tubing to the analyser. The analyser and Testoterm were both calibrated against the certified bottled standard gas prior to and after sampling.

### *Particulate emissions (PM$_{10}$)*

PM$_{10}$ emissions were determined using a Graseby Andersen in stack six stage cascade impactor. This piece of equipment is easily attached to the isokinetic sampling line commonly used for total particulate emission measurements[8] in which the flue gas sample is drawn through a single filter and all particulates are captured on it. The impactor consists of a series of six stainless steel collection plates each with a pattern of progressively smaller holes, cross-hair gaskets to ensure the filter papers remain correctly positioned on the collection plates during a run, spacers to ensure the correct distance is maintained between plates, a back up filter to capture any very fine particulates that pass through all the stages and a preseparator unit to remove any large particulates (greater than approximately 15 microns) prior to entry of flue gas into the impactor. The impactor works on the principal of aerodynamically and automatically classifying particulates into six size ranges based on the inertia of the particulates. The size of particulate collected on each stage is determined by several factors including viscosity of incoming air, particle density, velocity of aerosol jet and jet diameter.

The methodology for use of the impactor is in accord with guidelines supplied by the manufacturer and described as being "an EPA type methodology." The EPA method referred to is USEPA Method 201A "Determination of PM$_{10}$ emissions from stationary sources - constant sampling rate procedure." The single most critical factor in operating the impactor is to ensure that a constant known flow (of between 0.1 and 0.7 scfm) passes through the impactor for the entire sampling period. Variations cause alterations in the cut points for each sampling stage and may give misleading results. Factors such as excessive moisture in the flue gas, clogging of filters, overloading of filters and variations in stack gas velocity can all bring about variations in flow through the impactor.

In order to perform an acceptable PM$_{10}$ measurement it is necessary to carry out a number of preliminary steps. These include selection of sampling site (as per ASTM D 3685-78 - the method used for carrying out a total particulate measurement) and performance of a total particulate loading test. This includes full stack traverses to establish a velocity profile for the stack and enable appropriate nozzle size(s) to be selected and an estimation of sampling time to be made for the impactor test. Ideally no more than 10 mg of sample should be collected on any

of the six stages in the impactor. Beyond this weight, entrainment may begin and result in a shift of size distribution.

Preparation of the cascade impactor is a rather meticulous process involving thorough and careful cleaning of all collection plates, cross-hair gaskets and spacers, pre-conditioning and weighing of the filters and accurate assembly of all the components into the outer shell of the impactor. Disassembly of the impactor after the test is also attention demanding as it is essential that no material on any of the filter papers is lost prior to reweighing. The actual running of the test itself is very much the same as carrying out a normal total particulate measurement. From the recorded field data (gas flow rates, sampling temperatures and other variables) and calibration graphs supplied by the equipment manufacturer it is possible to calculate cut points for each impactor stage and these, combined with the weight of sample collected on each stage, allow for the weight percent of material within each size range and cumulative weight percent less than each size range to be calculated. A graph of particle size against the function log 100/(100-cumulative weight percent) is plotted and the best fit straight line for the six points is determined mathematically. From this graph the weight of $PM_{10}$ material may be calculated.

In some instances, the particulates captured on the single filter used for a total particulate measurement (by Method ASTM D 3685-78) were removed from the filter taking care to avoid, as much as possible, removal of any of the filter material itself. The particulates were suspended in an appropriate liquid (usually water) and dispersed by ultrasonic treatment. The size distribution of the resulting particulates was then determined using laser diffraction and compared with the distributions recorded by the cascade impactor.

## RESULTS and DISCUSSION

### *Emissions of toxic volatile trace inorganics*

The percentage recoveries for a range of trace elements from twelve combustion trials carried out on the laboratory combustion rig is shown in Table 1. It can be seen that generally speaking the recoveries were better than 60% - the only element being consistently lower than this was selenium.

The partitioning of the trace elements arsenic, boron, mercury and selenium between bottom ash, fly ash, particulate ash and flue gas and their concentrations in each component are shown for representative runs in Tables 2-5.

In none of these runs was the percentage recovery of arsenic, boron or selenium from flue gas greater than 2% of the amount originally fed in. On the other hand for mercury the majority of material was recovered from the flue gas.

*Table 1 Recoveries (as percentage of amount fed) of volatile toxic trace elements from combustion\* of sub-bituminous industrial coals (50kW laboratory combustion rig)*

| Run | 1 | 2 | **3** | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| As | 72 | 90 | **74** | 99 | 129 | 140 | 15 | **64** | 89 | **87** | **90** | 104 |
| B | 81 | 83 | **67** | 90 | 103 | 93 | 77 | **65** | 92 | **67** | **102** | 101 |
| Cd | 69 | 120 | 82 | 80 | 73 | 120 | 82 | 93 | 106 | 38 | 51 | 45 |
| Cr | 77 | 119 | 73 | 129 | 122 | 108 | 90 | 30 | 102 | 51 | 103 | 94 |
| Cu | 66 | 121 | 120 | 120 | 105 | 111 | 83 | 81 | 86 | 51 | 130 | 70 |
| Pb | 88 | 85 | 88 | 92 | 83 | 96 | 83 | 30 | 140 | 24 | 25 | 54 |
| Hg | 68 | 69 | **65** | 51 | 55 | 108 | NM | **60** | 89 | **68** | **67** | NM |
| Se | 58 | 52 | **51** | 55 | 36 | 110 | 21 | **19** | 45 | **16** | **28** | 54 |
| Zn | 100 | 103 | 96 | 104 | 124 | 106 | 90 | 39 | 34 | 52 | 24 | 83 |

*\*All runs are sub-bituminous on the underfeed stoker except for 3 and 4 (fluidised bed) and 12 (biomass on stoker).*

*Table 2  Partitioning of selected trace elements for Run 3 (sub-bituminous coal, fluidised bed combustor).*

| | Bottom ash μg/g (% of element) | Cyclone ash μg/g (% of element) | Filter ash μg/g (% of element) | Flue gas μg/dsm$^3$ (% of element) |
|-----|-----|-----|-----|-----|
| [B] | 350 (10) | 4600 (51) | 12000 (5) | 188 (1) |
| [As] | 5.5 (39) | 11 (30) | 38 (4) | 0.49 (0.4) |
| [Se] | 0.0 (0) | 3.7 (34) | 49 (17) | 0 (0) |
| [Hg] | 0.007 (1) | 0.18 (8) | 0.71 (1) | 4.5 (55) |

*\* dsm$^3$ = dry standard cubic metre (273 K, 101.3 kPa)*

*Table 3: Partitioning of selected trace elements for Run 8 (sub-bituminous coal, underfeed stoker combustor).*

| | Bottom ash μg/g (% of element) | Cyclone ash μg/g (% of element) | Filter ash μg/g (% of element) | Flue gas μg/dsm$^3$ (% of elementl) |
|-----|-----|-----|-----|-----|
| [B] | 3470 (60) | 5270 (2) | 4400 (1) | 698 (2) |
| [As] | 5.5 (35) | 220 (28) | nm | 0.82 (1) |
| [Se] | 0.75 (11) | 22.0 (6) | nm | 0.77 (2) |
| [Hg] | 0.03 (2) | 7.3 (10) | nm | 3.7 (47) |

*\*nm = not measured*

*Table 4: Partitioning of selected trace elements for Run 10 (Sub-bituminous coal, underfeed stoker combustion)*

|  | Bottom ash µg/g (% of element) | Cyclone ash µg/g (% of element) | Filter ash µg/g (% of element) | Flue gas µg/dsm$^3$ (% of element) |
|---|---|---|---|---|
| [B] | 1700 (60) | 5400 (4) | 11000 (2) | 202 (1) |
| [As] | 11.6 (58) | 230 (29) | nm | Not detected |
| [Se] | 0.75 (7) | 34 (8) | nm | 0.32 (1) |
| [Hg] | 0.05 (2) | 6.2 (12) | nm | 4.3 (54) |

*Table 5: Partitioning of selected trace elements for Run 11 (Sub-bituminous coal, underfeed stoker combustion)*

|  | Bottom ash µg/g (% of element) | Cyclone ash µg/g (% of element) | Filter ash µg/g (% of element) | Flue gas µg/dsm$^3$ (% of element) |
|---|---|---|---|---|
| [B] | 6800 (99) | 2600 (2) | 3200 (1) | 23 (0.2) |
| [As] | 24 (39) | 510 (51) | nm | Not detected |
| [Se] | 0.95 (8) | 35 (18) | nm | 0.71 (2) |
| [Hg] | 0.02 (2) | 0.06 (6) | nm | 5.2 (59) |

In several instances there was an appreciable amount of unaccounted for arsenic, boron and selenium. There may be a number of reasons why this is so - deposition or condensation onto walls of the combustion rig, variations in feedstock or failure to capture the trace elements effectively in the impinger solutions are possibilities - and statements about the relative importance of each contributor need to be made cautiously.

It is worth noting that boron is not among the trace elements specified for Method 29 and this originally suggested that, for this element at least, the above result was not reliable and significant quantities could be escaping in the flue gas. However for other runs (incuding run 12) in which a completely different solid fuel, bark, was burned on the same laboratory combustion rig, boron recoveries of close to 100% were obtained with significant quantities being associated with flue gas (35%) and fly ash (55%) and comparatively small amounts remaining trapped in bottom ash (11%). In this run the actual concentrations of boron in the flue gas (275 µg/dsm$^3$) was similar to that seen in some of the coal trials and its concentration in the impinger solutions was quite low (900 ppb) compared with up to 2700 ppb for some of the coal runs. It is unlikely that this is due to saturation of the impinger solution because over 90% of the boron is normally recovered from the first impinger in the line with less than 10% being recovered from the second.

The reason for the low boron (and arsenic and selenium) concentrations in flue gas is probably mainly related to loss of the elements by deposition within the combustion unit. Certainly for the highly alkaline (high calcium) sub-bituminous coals used in these runs it has been shown[9,10] that inclusion of boron into calcium alumino-silicate matrices is an important factor in the high retention levels seen for this otherwise volatile element. These calcium alumino-silicate matricies may be deposited in the combustion unit and not measured in the mass balances. The reaction becomes increasingly prevalent above 950°C - a temperature which is readily exceeded in stoker combustion (Run 8) but is above that used in the fluidised bed (Run 3). The

result is a much greater retention of boron in the bottom ash of the stoker runs than the fluidised bed runs. Runs 10 and 11 were performed on samples of coal from the same seam but with rather different ash mineralogies - one of which was particularly conducive to boron retention (run 11) the other significantly less so (run 10). Reactions between calcium oxide and volatile arsenic and selenium oxides are also likely to account for retention of significant amounts of these elements and may also lead to deposition of arsenic and selenium containing material throughout the combustion apparatus. In the case of bark samples, the calcium concentrations are very low, little calcium alumino-silicate forms, most of the boron escapes the combustor and a significant quantity reaches the flue gas where it is trapped quite efficiently by the nitric/peroxide impinger solutions.

Much of the "missing" mercury is also likely to be trapped within the combustion apparatus rather than escaping the impinger solutions. Again the majority of the captured mercury was found in the first permanganate/acid impinger with comparatively small quantities being recovered from the second. It was found that the cyclone and filter ashes had reasonable mercury capture ability - probably due to their high levels of unburnt carbon (20 to 35%) and the significant amount of microporosity in the 5 to 50 Angstrom diameter range where good mercury ($Hg^0$) capture efficiencies are expected[11].

### *Emissions of sulphur dioxide*

The comparative results for sulphur dioxide monitoring by USEPA Method 6, Testoterm 350 and pulsed UV fluorescence methodologies are shown in Table 6.

*Table 6: Comparison of $SO_2$ emission levels as determined by three methodologies*

| USEPA Method 6 [$SO_2$] ppm | Testoterm 350 [$SO_2$] ppm | Pulsed UV [$SO_2$] ppm |
|---|---|---|
| 1720 | 1850 | nm |
| 2472 | 2552 | nm |
| 2477 | 2493 | nm |
| nm | 86 | 92 |
| nm | 40 | 44 |
| 144 | 135 | 121 |
| 79 | 70 | 74 |

*\* nm = not measured,*

The results from the Testoterm and pulsed UV fluorescence analyser are mean values taken over the 30 to 60 minute USEPA Method 6 sampling period. This sampling period was always chosen to coincide with, to as great a degree as possible, a time of steady plant operation. Agreements between methods are within 10% of each other for the four low emission cases and for the high emission cases extremely good agreements are seen between the Method 6 and Testoterm methods.

It was possible to carry out sulphur inventories for many of the industrial runs and, using the proximate, calorific value and sulphur values of the coals, to calculate the theoretical emission concentrations associated with its combustion. In all cases the measured emission values were lower than the theoretical - by up to 30% in some instances. The discrepancies arise from a

number of causes including retention of sulphur in ash, incomplete combustion of coal, heterogeneity of feedstock coal, adsorption of sulphur dioxide downstream of the combustor and prior to reaching the flue and measurement errors.

The good agreement between emission levels suggests that errors due to measurement are a minor contributor. For the laboratory runs almost complete sulphur inventories were obtained (between 86 and 102% recovery) and a considerable degree of sulphur was recovered with the bottom and cyclone ash. The greatest amount was seen for a low temperature (800°C) fluidised bed run (Run 3). In this instance the bottom and cyclone ashes accounted for 61% of the total sulphur and the flue gas $SO_2$ concentration corresponded to the release of only 30% of the sulphur fed in with the fuel (none was fed in with the fluidising sand). The same coal burned on an underfeed stoker unit (Run 8) retained 23% of the sulphur in the bottom ash and emitted 63%. The reasons for this finding are detailed elsewhere[10] but basically relate to the well documented ability of calcium oxide to capture sulphur dioxide and the extent to which conditions within the combustor favour the process. In Run 11 where a comparatively low calcium content coal was used, and other influencing factors were present,[9] 95% of the sulphur fed in was released in the flue gas. What the findings show quite clearly, apart from the fact that several suitable methods are available for sulphur dioxide emissions monitoring, is that the emission levels are very sensitive to coal properties and combustion regime and it is a significant oversimplification to assume that a constant percentage of sulphur in the feedstock will always be released in the flue gas.

### *Emissions of particulates (PM$_{10}$)*

The levels of total particulate emissions as measured by a single filter method and by the six stage cascade impactor are in good agreement across a wide range of loadings (from 100 to 600 mg/dsm$^3$) as shown in Table 7.

*Table 7: Total particulate emission levels as measured by ASTM method and cascade impactor*

|  | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 | Site 8 |
|---|---|---|---|---|---|---|---|---|
| ASTM | 219 | 228 | 521 | 121 | 78 | 677 | 354 | 139 |
| Cascade Impactor | 223 | 245 | 496 | 131 | 107 | 550 | 394 | 146 |
| %PM$_{10}$ | 85 | 71 | 52 | 60 | 63 | 46 | 63 | 65 |

The data in Table 7 is from a few selected sites only but is representative of that from all sites measured. Overall the mean variation between the two methods is 10.4% and there is no obvious bias in the data. The %PM$_{10}$ emission factors (mean value 63%) are similar to those cited by the USEPA[12] (55 to 65%) for stoker type firing systems with inertial grit arrestors such as those found in the majority of New Zealand industrial plant.

Another feature to emerge is that operations with more efficient emission control systems are better able to capture the larger particulates but in doing so they increase the percentage (although not the amount) of small particulates escaping with the flue gas. It is often misleading

to judge a system by the percentage $PM_{10}$ readings it reports.  A corollary of this is that, generally speaking, as total particulate levels decrease there is a tendency for the values for total particulate and $PM_{10}$ to converge.

In a few instances particulates were recovered from the single filter used to carry out the ASTM total particulate test and analysed by laser diffraction - a somewhat less tedious and meticulous method than that associated with the cascade impactor.  The most obvious feature was that size distributions for the total particulate test material tended to be clustered toward the higher end of the size scale ranges - a consequence of agglomeration only partially resolved by ultrasonic treatment. Typically the smallest size range from the impactor covered 0 to 0.6 µm and anywhere from 0 to 50% particulates were captured there.  Less than 5% of the total particulate test material fell into this range.  Typically the fifth size range covered particulates of approximately 5 to 7 µm.  Between 1 to 20% of the impactor material was found there whereas up to 35% of the total particulate test material may be found.  The sixth stage normally captured material in the 7 to 17 µm range and accounted for less than 10% of the total. Frequently 20 to 40% of the total particulate test material fell in this range.

In order to get a truer picture of the total size distribution of particulates in flue gas the impactor method, although rather time consuming and meticulous, is greatly superior. However the actual value for $\%PM_{10}$ as determined by laser diffraction size analysis of total particulate test material showed reasonable agreement with that obtained by the cascade impactor method.  For three sites where $\%PM_{10}$ comparisons were made the impactor method gave 47, 58 and 65% $PM_{10}$ while the corresponding values for recovered material were 70, 66 and 75%.

## CONCLUSIONS

USEPA Method 29 appears well suited to measurement of boron concentrations in flue gas from combustion sources even though boron is not among the elements specified in the standard. This is important in the New Zealand context as boron is the one trace element regularly found in New Zealand coals at moderate to high concentrations.

The reason for the small percentage of boron, arsenic and selenium released in flue gas relates mainly to the highly alkaline nature of the coals and the stoker type firing systems used to combust them and not to the inability of the method to capture it.

The highly volatile element mercury is among those included in Method 29 but typically less than 70% is captured.  Capture by fine ash particulates with high unburnt carbon contents probably accounts for much of the remainder.

The wet chemical USEPA Method 6 is the one often stipulated for measurement of sulphur dioxide emission levels from combustion sources but less cumbersome non-standard methods based on electrochemical Testoterm 350 and pulsed UV fluorescence techniques match the Method 6 results to within 10% and often within 5%.

Sulphur partitioning behaviour was also influenced by the highly alkaline nature of the coals and was sensitive to combustion regime.  It is a significant oversimplification to assume that a

constant percentage of any of these elements in the feedstock will be released into flue gas and any conclusions based on it may well be extremely inaccurate.

Total particulate and $PM_{10}$ emission levels as measured by an in stack six stage cascade impactor (Method USEPA 201A) agreed closely with total particulates as measured by the single filter standard ASTM method and reasonably closely in terms of percentage $PM_{10}$ material recovered from the single filter. However the size distributions as recovered from the single filter were biased toward the larger sized fractions as a result of agglomeration of particulates and do not give an accurate picture of the size fractions exiting with flue gas. If this is required for whatever reason (regulatory purposes, designing improved grit arrestors or fine tune existing equipment to meet specifications) then the cascade impactor method, although much more meticulous and difficult, is much superior.

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